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Influence of Physical Characteristics of Batch Materials on Glass Melting Processes and Quality

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INTRODUCTION

Specifications limiting the permissible variation of chemical and physical specifications of the various raw materials used in glass batches are quite familiar to the suppliers of these materials. While this paper is not directed to these suppliers, it might well be, as its purpose is to show the reason for the specifications they must strive to meet. That there are reasons must be apparent to them as there would be about as many different specifications on the same materials as there are consumers if it were possible. This indicates different philosophies and ideas pertaining to what happens, what is desirable, or what must not happen in a glass tank which is converting these materials into a glass.

This paper then, will show the purpose of the raw material specifications currently being employed by the Brockway Glass Company.

CHEMICAL CHARACTERISTICS

It is our belief that the key to a successful glass production operation is consistency of glass processed. All plants have a theoretical glass composition which works very well, at least some of the time. Most techniques used to control the glass composition such as density, softening point, coefficient of expansion, etc., are measurements designed to detect changes. If none of these properties changed we could safely assume that none of the production troubles were resulting from glass composition changes.

In order for such a composition control program to work, it is essential that the glass composition changes caused by raw material composition changes be less than normal control limits found typical for the various properties being measured. Our practice is to set specifications so that the greatest individual oxide variation permissible itself will only change the density one-half of 3-sigma control limit. This works out to be about ±.3% to .5% for most oxides.

PHYSICAL CHARACTERISTICS

It is not as simple to define the effect of variations of physical characteristics of raw materials. Even when it is possible to specify the particle size desired on the basis of known effects in the batch or melt, it is not usually possible to economically produce the raw material with the desired optimum screen analysis. The natural grain size, hardness, and friability of the raw material usually determines what size distribution will result when it is processed. If certain size fractions naturally resulting from the processing are not desirable for glass manufacturing, then the producer must have another outlet for this material or it is usually too uneconomical or impractical to produce as specified.

Therefore, specifications or screen analysis of any raw material must be a compromise between what is thought

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to be ideal and what is practical to produce. Cost usually determines the practicality of the choice.

EFFECT OF PARTICLE SIZE

In order to know the kind of compromise that is preferable, however, it is necessary to know what effects that various particle sizes of the batch ingredients will have on batching and melting.

These effects probably can be classified in three general categories; ie., batch mixing and segregation, melting and fining, and tank life. In order to arrive at sensible specifications for screen analyses of various materials, quantitative information on the effect of particle size on each of the above categories is necessary. With these data, it is possible then to not only derive reasonable specifications but to modify the operations themselves in which these variables are involved so that the particle size range is not as critical to the operation. This latter possibility is the most important as in most cases, the ideal screen analysis from all three standpoints is not available, and the operation itself is the simplest to modify.

MIXING AND SEGREGATION

It has been known for some time that for maximum mixing efficiency and a minimum tendency toward demixing or segregation in subsequent handling of the mixed materials, the particle sizes of all materials in the mix should be as similar as possible. The screen analysis of sand usually determines the screen analyses of other materials to be mixed with it. The screen analyses of the sand in turn is based on its natural occurrence plus screening to remove coarse particles (±20 mesh) which are too difficult to dissolve in the melt and the fines (–200 mesh) which cause difficulty in handling or are lost by dusting.

Provided a reasonable match of the other materials to the sand is maintained, especially in the extreme size ranges, good homogeneity of mixing can be obtained with modern equipment in 3 to 5 minutes for a 2 ton batch. Use of cellular bins or unit batch handling will usually minimize segregation during handling to a point where it is not troublesome.

The range of screen analyses for all the materials can be greatly extended, however, if damp batches are used. If 4 to 5% moisture is maintained in the mixed batch, it can be stated that no segregation will occur regardless of how it is handled. Obviously, special techniques for mixing, handling, and feeding batch this wet must be worked out, but the advantage that results, not only from a segregation standpoint, but also from melting and tank life improvements make it quite worthwhile. Most of the data which is presented in this paper was actually obtained in efforts to evaluate the effects of wet batches. As far as segregation is concerned, it is obvious that if the batch is damp, rolling is prevented and consequently segregation is prevented. The most startling part about this is how much segregation is taking place from dry batch in an operation using modern techniques supposed to prevent it. This batch segregation was missed when the conventional long hand technique of acid solubles, water solubles, etc., was used to determine it. A rapid method using the measurement of the electrical conductivity of the liquid in which a known weight (100 gm/500 cc) of batch sample was dispersed was devised which made it possible to make determinations of alkali in the batch to within ±.5%.

Average segregation results from two types of batch plants and handling systems before and after addition of water to the batch showed a remarkable improvement with the wetter batch. Unclassified soda ash was being used at the time.

The range of segregation determined in a 24 hour period from hourly samples taken at the furnace for the system using conveyor handling and a cellular storage bin with dry batch (actually 1.5% moisture) based on a theoretical content of 17.0%, was ±7% alkali. After increasing the moisture to 3%, the segregation in terms of alkali range was only ±.5%.

The typical range in a system using unit batch cars for the same period was ±2% for dry batch and zero to ±.2% for moist batch.

The real significance of these figures is best demonstrated if the % alkali segregation is converted to pounds of soda. For example, in the last case where the variation in alkali was found to be ±2%, this is equivalent to a variation in soda ash of ±80 pounds. The alkali content of the total batch will, of course, be correct but during the discharge of this batch from the hopper to the furnace there are times when the batch being fed is actually over or short the equivalent of 80 pound of soda. Bear in mind that this is occurring in a unit batch system which is undoubtedly best from a segregation standpoint. In the preceding case of batch being delivered from a cellular bin, the variation is of longer duration and is equivalent at times to about 300 pounds of soda ash. Such fluctuations in batch composition during a day are bound to have their effects on the homogeneity of the emergent glass. By practically continuous batch analyses (every 15 minutes) around the clock correlated with homogeneity measurements on the finished glass, it was possible to observe variation in homogeneity corresponding to the observed changes in batch composition. It was possible also to predict the arrival time of a cordy period, its duration, and the magnitude and intensity of the stresses.

Needless to say, the use of the moist batch eliminated these changes and is now standard operation.

The most significant result from the use of moist batch is not that segregation is eliminated with properly sized materials, but that it is also eliminated for improperly sized materials. In other words, it is possible to use fine material, coarse materials, even coarsely crushed cullet, without having them separated in the batch.

The advantages to this increased flexibility in the choice of raw material particle sizes makes it possible to use lower priced materials, as tight screen specifications result in a higher cost. Melting and fining advantages can also be obtained from the use of finer ground materials.

MELTING AND FINING

There are many papers in the literature concerned with the effect of particle size of various ingredients on melting and fining rates. It is sufficient to say here that particle size does affect melting and fining rates. Generally, the finer the material the faster it will melt or dissolve. Moist batch also has a beneficial effect on these

rates. The viscosity of the glass is also lowered with increased moisture content. Advantage of all these can be taken if finer grained materials can be used.

TANK LIFE

The greatest deterrent in the past to the use of fine grained batch ingredients is the dusting and carry-over loss which adversely affects furnace life. This is one of the most important factors in setting up raw material screen analyses specifications. They must be so chosen that a minimum carry-over from the batch to the furnace refractories can occur for the particular operation concerned. Feeding equipment and furnace operation are also concerned, but carry-over is the deciding factor in furnace life.

Since the introduction and usage of electro-cast refractories in the melter, sidewalls, and bottoms, under the metal-line life of refractories has been extended tremendously. The new weak spots are superstructure, crowns, checkers, port necks, etc.

It can be shown that the attack on these parts is directly related to the amount of composition of dust lost from the batch.

In fact, a calculation of the flux composition attacking the refractories and depositing as slag on the checkers and in the tunnels can be made from chemical and physical characteristics of the raw materials alone. Actual chemical analysis of these corrosive slags are within experimental errors of the predicted compositions.

By assuming a constant gas velocity over the batch and considering the densities of the various raw materials, it can be shown that the fines which can be expected to be lost from the furnace are the minus 170 mesh sand, −120 soda ash, −170 mesh limestone, dolomite stone and fluorspar, −140 mesh syenite, feldspar and calumite, and −200 mesh barytes.

From the screen analyses of these various materials, and their amount in the batch, the amount of each ingredient which can be considered as a potential loss from each batch can be calculated. The actual amount of this mixture which will be lost will vary from tank to tank depending on comparative flame velocities, type of batch feeding, moisture content in batch, tonnages, temperatures, and rate of fritting. An index of the amount actually lost can be determined by weighing the material cleaned out of the tunnels periodically, or by extracting dust samples from the furnace continuously with a cyclone collector. Quantity and composition of the dust is then recorded at frequent intervals.

Proof that the carry-over material is primarily responsible for the slagging action is best shown by an example of actual data on a furnace in operation.

In the first case, the top brick on a course of checkers was removed, a section of the slagged portion cut out, and the total analyzed.

The flux composition predicted on the basis of fines in the batch materials is:

SiO_2	20.42%
R_2O_3	4.94
CaO	15.38
MgO	1.37
BaO	1.94
Na_2O	53.53
K_2O	.54
S	.17
F	1.45
MnO	.26

Utilizing the known analysis of the brick, it was determined on the basis of the R_2O_3 content in the section analyzed that this section contained 83% brick and 17% flux.

Calculating the sample analysis from the predicted flux composition and its concentration in the brick gives the following:

	Analysis of Surface of Attacked Brick	
	Calculated	Actual
SiO_2	25.40%	21.04%
R_2O_3	60.40	65.90
CaO	3.09	2.30
BaO	.46	.44
Mgo	.39	.22
Alkali	10.25	10.04

The second case chosen for an example is a little more complex but again reveals the importance of the screen analysis of the materials.

Here, tunnel debris under basic checkers was analyzed with the following results:

SiO_2	11.90%
R_2O_3	.55
CaO	1.08
BaO	.50
Mgo	1.94
Na_2O	32.49
K_2O	5.21
SO_3	46.08
F_2	.04
Cr_2O_3	.25
Fe_2O_3	.20

The analysis of the basic brick in the checkers is known to be:

SiO_2	6.90%	MgO	65.81%
Fe_2O_3+FeO	5.89	Cr_2O_3	8.57
Al_2O_3	10.00	SO_3	.99
CaO	1.83		

Utilizing the chromic oxide in the brick as an index to the amount of brick in the slag, we find that 3% brick must be present.

The brick analysis is then converted to its oxide contribution in the slag as:

SiO_2	.21%	MgO	1.97
Fe_2O_3+FeO	.18	Cr_2O_3	.26
Al_2O_3	.30	SO_3	.03
CaO	.05		

Assuming that the sulfates present were all formed from alkali vapor from volatilization reacting with sulfates in the combustion products, we find that 35.70% alkali will be tied up with the 46.0% SO_3 present. Thus all but 15.3% of the original slag analyses has been accounted for; which must be the dust contribution.

The dust composition based on screen analyses, material densities and relative amounts of each in the batch shows it to be:

SiO_2	74.37
R_2O_3	3.14

(*Continued on page* 226)

Glass Division Schedules Twenty-Two Papers for Annual A. C. S. Meeting

• FOR THE FIRST TIME in its 59-year history the American Ceramic Society will hold its national meeting in Texas with the Statler Hilton in Dallas as headquarters for registration and most of the meeting activities.

Appropriately, two Texans will have prominent roles in the five day meeting to be held May fifth to ninth.

Speaker at the annual banquet will be John Ben Sheppard, well know Texas attorney and political leader, who recently returned to private law after four years as attorney general of Texas.

Robert L. Stone, University of Texas instructor and a member of the meeting planning committee, will be installed as Vice President of the Society's Ceramic Educational Council.

Some eighteen hundred members representing the glass and ceramic industries are expected to attend this 59th Annual Meeting.

Among the special events of the meeting will be the installation of the Society's national officers for 1957-58 and elevation of twenty-three men and one woman to the stature of Fellows for their outstanding contributions to ceramic science.

"Creativity" by the National Institute of Ceramic Engineers, an affiliate of the Society, will be another special feature of the program.

Professor Farrington Daniels, Chairman of the Chemistry Department of the University of Wisconsin, has been chosen to deliver the Edward Orton, Jr. Memorial Lecture. Professor Daniels' topic will be "The Utilization of Solar Energy."

John F. McMahon, Dean of the State University of New York, College of Ceramics at Alfred University will be installed as president of the American Ceramic Society for the 1957-58 term.

Dean McMahon joined the Society in 1925 and was elected a Fellow in 1937. Born in Cohoes, New York

J. F. McMahon

on October 1, 1900, Dean McMahon attended Alfred University, receiving a B. S. degree from the Department of Ceramic Engineering in 1923. After spending a year at Alfred as an instructor, he was employed at Queen's Run Refractory Company, Lock Haven, Pa. In 1925, he joined the Ceramics and Road Materials Division of the Canadian Department of Mines.

After eleven years in this work, Dean McMahon returned to education at Alfred as assistant professor of research. In 1944 he was appointed Professor of Ceramic Research, and in 1948 he was made Associate Head of the Research Department. He became Dean of the College of Ceramics the following year.

O. L. Anderson

Orson L. Anderson, Bell Telephone Laboratories, Murray Hill, N. J. will be installed as Chairman of the Glass Division succeeding J. Earl Duncan, Pittsburgh Plate Glass Company, Research Laboratories, Creighton, Pa.

Leonard G. Ghering, Preston Laboratories, Butler, Pa., remains as Trustee of the Division and Fay V. Tooley, Professor

(*Continued on page* 229)

Current Japanese Concepts of Glass Structure

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I. HISTORICAL DEVELOPMENTS

E rly in this century glass was dealt with by our prog nitors as a supercooled liquid. The additive relation of some physical properties with oxide components hav been considered simply as the characteristic nature of s lution without touching on the details.

A the properties of glass at around the visco-elastic ran e were unveiled one after the other, and moreover, wit the brilliant success of the X-ray method in investigati g the structure of glass during the second and third dec des, the problem of exploring the nature of glass seer ed to have attracted our top level scientists who wer working in the academic as well as in the industrial fiel

I addition our industrial circles have gradually recogniz d the usefulness of the structural concepts for solving many important technical problems, which has led to the investigations of this basic science.

Until the end of the third decade, however, few theories were put forward among us which were comparable with those advanced continuously in other countries.

In approaching the study of the structure of fused silica H. Yamamoto and S. Suetoshi[1] used in 1938 the method of electron diffraction. Contrary to the opinion of Shishakov[2] the analysis resulted in the admission of the random-network structure.

The chief difficulty in carrying out the study of glass structure by electron diffraction may be the electrical charge on the sample which distorts the pattern completely. H. Kamogawa[3] succeeded in removing such charges by applying another low electron beam. By this method he unveiled the nature of the glass surface the structure of which was found to be somewhat different from the interior. Although the nature of the surface of glass is being studied intensively by S. Tsuchihashi[4] and others the direct approach by electron diffraction has been put aside.

An approach to the glass structure from mol refraction and volume was made by T. Abe[5]. Concentrating the attention to the role played by the two kinds of oxygen, namely, bridging, and that of bonding with metallic ion he derived a formula representing the mol refraction of SiO_2-Na_2O-CaO glass in the same fashion as Kordes[6]

$$MR_{glass}=a_1 R_{Si}+2a_2R_{Na}+a_3R_{Ca}+2a_2R^{SiNa}+2a_3R_O^{SiCa}+(2a_1+a_2+a_3-2a_2-2a_3)R_O^{Si} \quad (1)$$

in which a_1, a_2, a_3 are the mol fraction of oxides, and R's are the increments of the refraction of respective ions. He confirmed that the above formula is good enough for $a_1=1\sim1/3$.

The relation between the ionic refraction and the molecular composition of SiO_2—Na_2O—CaO, and of SiO_2—K_2O—CaO glasses are reproduced in Fig. 1. The curves indicate that: (a) With the increase of the mol fraction of SiO_2, i.e. a_1, R_o^{SiNa} and R_o^{SiCa} decreases at first and, after passing through a minimum, tends to increase, while (b) R_o^{SiK} shows a marked increase at the beginning and then remains fairly constant until the curves turn upwards again. As the ionic refraction is the function of the distance of neighboring ions the above curves are of much interest.

Further he proved that mol refraction of $a_1B_2O_3$—a_2Na_2O glass may be represented by

$$MR_{glass}=2a_1R_B+2a_2R_{Na}+8a_2R_O^{BIII\,BIV}+(3a_1+a_2+8a_2)R_O^{BIII} \quad (2)$$

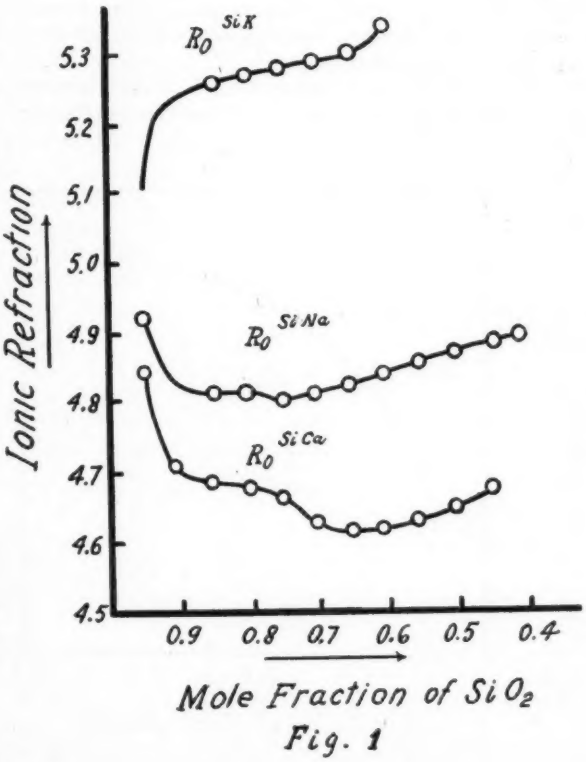


Fig. 1

where $R_o^{B^{III}\,B^{IV}}$ and $R_o^{B^{III}}$ are the ionic refractions, respectively, of O^{2-} coupling both the triangularly and tetrahedrally coordinated B^{3+}, and of that coupling with triangularly coordinated B^{3+} at this point.

In the nineteen-forties U. Yoshida[7] advanced a new theory. Tracing an analogy with the structure of water, in which according to Stewart[8] microcrystals of ice

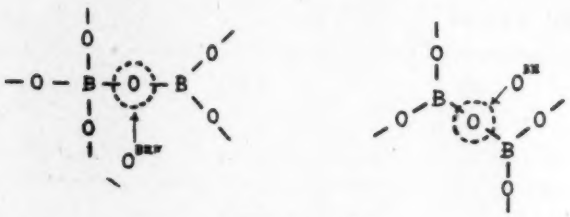


Fig. 2

of the order of unit cell are momentarily appearing and disappearing, he assumed that glass is composed of such cybotactic crystals and free molecules as shown in Fig. 4. Assuming that equilibrium is established between the number of cybotactic crystals, n, and that of free molecules, so that

$$\alpha(N-xn)=\beta xn$$
$$n=N/x(1+\beta/\alpha) \qquad (3)$$

where N is the total number of molecules in unit volume, x the number of molecules in a cybotactic crystal, and α, β are constants. Assigning to α and β the negative and positive temperature dependency, respectively, he was able to give the qualitative explanation of such properties as viscosity, electrical conductivity, devitrification, and rupture of glass.

During this period T. Moriya[9] published successively a number of papers which cover the vast field of his studies on the solubility, viscosity, electrical conductivity, and dielectric loss of binary and ternary glasses.

He measured, for example, the solubility of Na_2O—SiO_2 glasses containing various amounts of Na_2O, at different temperatures. It was found out that log ($M\times 10^7$), in which M is the gram-molecules of Na_2O dissolved out from unit area, may generally be represented by sets of two straight lines intercepting at about $1/T\times10^4=30$ when the values are plotted against the reciprocal of absolute temperatures. From the results

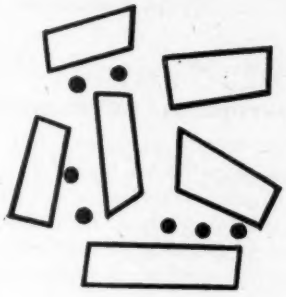


Fig. 4

the activation energy was worked out whose values gave a profound maximum at the composition $Na_2O{\cdot}2SiO_2$ as shown in Fig. 5.

In short he gathered the many evidences which indicate the sharp turning points in curves representing some physical and chemical characteristics of some definite compositions.

He thus advanced a theory of glass structure stating that glass generally consists of two patterns, one the micro-micel being made up of several hundreds of more atoms, and the other the separate atoms and molecules encircling the micro-micels, and that they are in equilibrium with respect to temperature. In a simple glass consisting of N molecules and containing μ micro-micels which is an assembly of n molecules there exists a relation

$$(N-n\mu)=Kn\mu$$
$$\text{or } K=(N-n\mu)\,1n\mu \qquad (4)$$

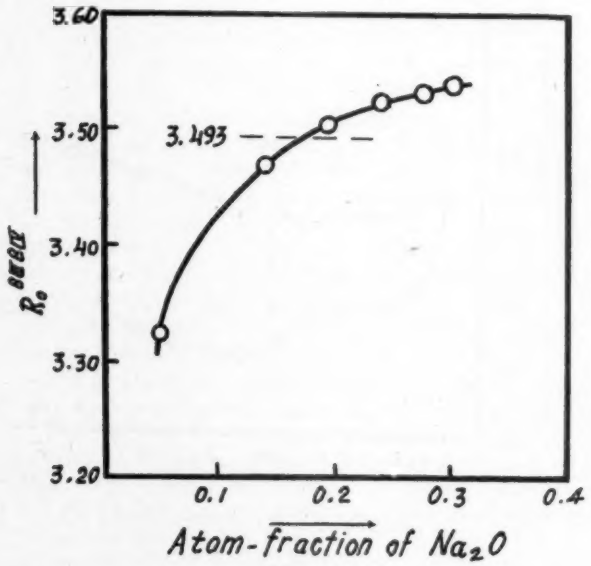


Fig. 3

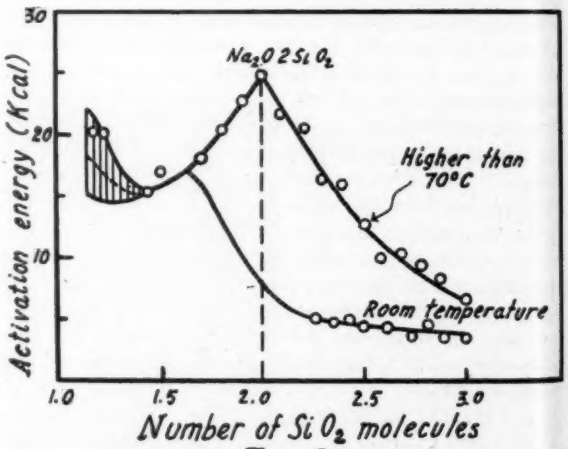


Fig. 5

where K is an equilibrium constant whose value decreases with decreasing temperature.

At first sight his theory might be regarded as being similar to that of U. Yoshida. However, the difference between the two rests in (1) that he assumed a random structure but assigned a fixed chemical composition to a micro-micel, and (2) that he allowed for the bond strength in the micel as being weaker than that in a regular crystal.

In Table 1 the chemical composition of probable micro-micels are consolidated.

Assuming this mozaic structure he proceeded to illustrate clearly the characteristic features of the viscosity, the electrical resistance, and the thermal conductivity of glass as well as the difference of viscosity between the quenched and annealed glass.

His picture of glass structure will be referred to later in some detail.

II. RECENT ACHIEVEMENTS

Dr. Abe and Prof. Moriya are now working actively on structural problems; the former on the structure of borosilicate glass and the latter on the viscosity of glass in the transition range. Furthermore, there are some excellent papers which have been published recently which go far towards solving the problem of glass structure.

Before introducing our recent achievements specifically, a list of the various subjects follows in order to allow us to observe our present activities. In Table 2 our current research subjects are itemized.

1. T. Moriya's Two Phase Theory of Glass Structure

As stated before Moriya considers that glass is composed of two phases, namely, one the amorphous "micro-phase" which he formerly called "micro-micel". Currently he seems to be concentrating his attention mainly to the rate of growth of size for proving his theory by comparing it with existing data on (1) temperature dependence and the time effect of the viscosity of glass, (2) the rate of strain release at a temperature in annealing range, and (3) the change of refractive index with time near the annealing range.

With regard to the structural change which may occur during the process of cooling of glass from the molten to the solid state he gave the following picture:

At sufficiently high temperatures molten glass might consist of the dissociated ions or molecules moving violently by thermal agitation. At lower temperature, however, such particles will begin to have the chance to associate, leading to the formation of the nuclei of micro-phase, presumably, by the driving force being eventually similar in nature to that acting for the formation of crystal structure. The number of the nuclei will increase with the decreasing temperature, and meanwhile the nuclei will gradually grow up to micro-phase.

Assuming that the energy of thermal elastic waves will be absorbed by micro-phases[10] which take the leading part in thermal conductivity of glass, Moriya estimated their average size with the result of 10^{-5} —10^{-6}cm, although they may have different shapes in compliance with different chemical composition.

The number and dimension of the micro-phase, however, may be considered to have different values according to the thermal history of glass. Namely, in glass quenched from higher temperature the micro-phases may have relatively small size leaving many dissociated ions around them. In well annealed glass, however, the size of the micro-phase may be fairly large, for the growth of the micro-phase will continue during the process of slow cooling by gathering the dissociated ions from the surroundings until they are saturated at transformation temperature.

In the temperature range below the transformation point micro-phases will begin to contact each other forming a dense packing. If the glass is heated above the transformation temperature the micro-phase will dissociate and their size will become smaller being always in equilibrium with respect to temperature.

It is considered that atoms in the micro-phase are vibrating around their definite equilibrium positions, while the dissociated ions are moving translationally like the Brownian movement of atoms in a liquid.

In the first and second part of his paper[10] the rate of the growth of a single micro-phase was considered, equal to the difference between N_1 and N_2, the numbers, respectively, of ions amalgamating to and escaping from the micro-phase referred to unit time and area, so that

$$dN/dt=S(N_1 - N_2) \qquad (5)$$

where S is the surface area of micro-phase being taken into consideration.

From this basic formula he worked out an equation which gives the volume of micro-phase, V_T, being an equilibrium at the temperature T as

$$V_T=A - Be^{-\Delta E/T} \qquad (6)$$

where $\triangle E$ is 1/K (K=Boltzman's constant) of the difference between the least kinetic energy necessary for the escape of an ion from the surface and the kinetic energy of the surrounding ions having the translational velocity

Table 1

Chemical Composition of Amorphous micro-micels

System	*Formulas of Probable micro-micels*			
$Na_2O{\cdot}SiO_2$	Na_2O —SiO_2	$Na_2O{\cdot}2SiO_2$	$Na_2O{\cdot}4SiO_2$	SiO_2
K_2O —SiO_2	$K_2O{\cdot}SiO_2$	$K_2O{\cdot}2SiO_2$	$K_2O{\cdot}4SiO_2$	SiO_2
Na_2O —CaO —SiO_2	$Na_2O{\cdot}SiO_2$	$Na_2O{\cdot}2SiO_2$	$CaO{\cdot}SiO_2$	SiO_2
Na_2O —CaO —MgO —SiO_2	$Na_2O{\cdot}SiO_2$	$Na_2O{\cdot}2SiO_2$	$CaO{\cdot}SiO_2$ $MgO{\cdot}SiO_2$	SiO_2

normal to the surface being just sufficient for the ion to be arrested in the micro-phase, and A, B are constants. He then formulated the volume V(t) of a micro-phase at the time t as

$$V(t)=V_T(1-e^{-at})+V_0e^{-at} \qquad (7)$$

where V_0 is the volume of the micro-phase at the time t=O, and a is a constant.

He then proceeded to formulate a viscosity equation which contains time and temperature as variables by assigning the volume of a micro-phase for the flow unit of the Eyring's[11] viscosity formula, and assuming that, in the annealing range, the elongation of a glass fiber is composed of the flow of micro phases and their visco-elastic deformation being represented by the Voigt model.

His theory was compared with the experimental result obtained by Lillie[12] as shown in Fig. 6.

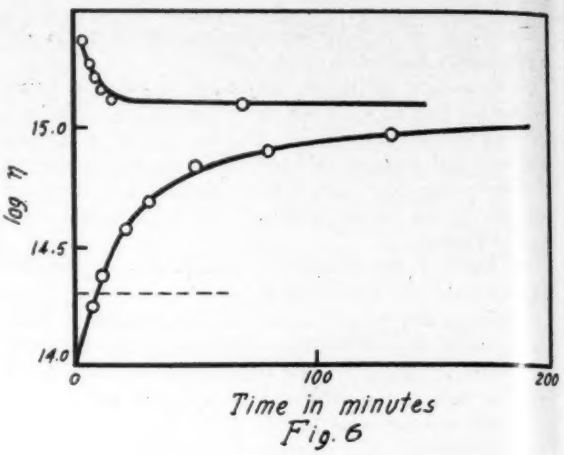


Fig. 6

Table 2

The Principal research subjects on glass structure in the last five years

Experimental background	Theory postulated	Author
Change of viscosity and refractive index with time.	Glass has a mosaic structure.	T. Moriya
Change of density with time at constant holding temperatures.	Time dependency of the density of glass at constant holding temperatures in annealing region may be attributed to the relaxation of elongated ionic distances being frozen in by quenching.	M. Mine
Rate of density change in transition region.	A thermodynamic approach regarding the flow and relaxation phenomena as being made up of the superposition of the network deformation and the vibrational motion around the configuration.	E. Kanai and T. Satoh
Relaxation phenomena in glassy high polymer.	A linear polymer theory based on the viewpoint that relaxation phenomena may be attributed to the general trend of chains whose elongation ratios tend to approach unity.	J. Furukawa
Viscosity, Expansion, and density of ternary borosilicate glasses	Law of the formation of atom groups in borosilicate glasses; the existence of XY_4, Y_3XXY_3, 2 XY_4 groups, in which X and Y represent, respectively, BO_3 and BO_4.	T. Abe
The difference between solubility of the quenched and annealed borosilicate glasses; change of expansibility with time.	Some characteristic changes of borosilicate glasses are attributed to the exsolution phenomena.	T. Tamura and Y. Mori
Induced absorption bands by X-ray irradiation and optical and thermal bleaching.	Existence of O^{2-} vacancies in the (SiO_4) network by which electrons are trapped. Positive holes trapped by alkali ion vacancies between neighboring oxygen ions.	R. Yokota
Flow at comparatively low temperature in an extensively quenched glass molten at different temperature.	Glass is characterized by the random spatial distribution of holes in a mass of glass which amalgamate or separate according to temperature change.	T. Yamate and S. Sakka

T. Moriya, Prof. of glass technology at the Tokyo Institute of Technology, Tokyo.
M. Mine, Prof. of ceramics at the Kyushu University, Fukuoka.
E. Kanai, Staff physicist of the Asahi Glass Co., Tokyo.
T. Satoh, Staff physicist at Physics Department, Safety Academy, Yokosuka.
J. Furukawa, Prof. of Polymer chemistry at the Kyoto University, Kyoto.
T. Abe, Staff physicist of the Laboratory of the Tokyo Shibaura Electric Co., Kawasaki near Tokyo.
T. Tamura, Y. Mori, Head and staff chemist of the Ceramic Division of the Government Research Institute, Osaka.
R. Yokota, Staff physicist of Tokyo-Shibaura Electric Co.
T. Yamate, S. Sakka, Assistants at the Sawai Laboratory of the Institute for Chemicl Research, Kyoto University, Kyoto.

For the rate of strain release Moriya used an equation

$$-dS/dt=(G/\eta)S \qquad (8)$$

in which S is the strain in glass, η the viscosity, and G the rigidity. Substituting η with his viscosity equation, and integrating with a proper initial condition he obtained a solution representing log S in terms of time. It will be seen in Figs. 7 and 8 that the agreement with the experimental value is excellent.

To illustrate the change of refractive index with time near the annealing temperature Moriya postulated an idea that the properties of glass can be represented with the mean value obtained by the additivity relation of the properties of the micro-phases and the dissociated ion so that the refractive index of a glass will be given by

$$n=n_mN_m+n_iN_i \qquad (9)$$

where n_m and n_i are, respectively, the refractive indices of the micro-phase and dissociated ion and Nm, N_i are the total number of ions in micro-phases and that of dissociated ions in unit volume. He thus derived a first order rate equation which represents the influence of the rate of growth of micro-phases on the change of refractive index with time.

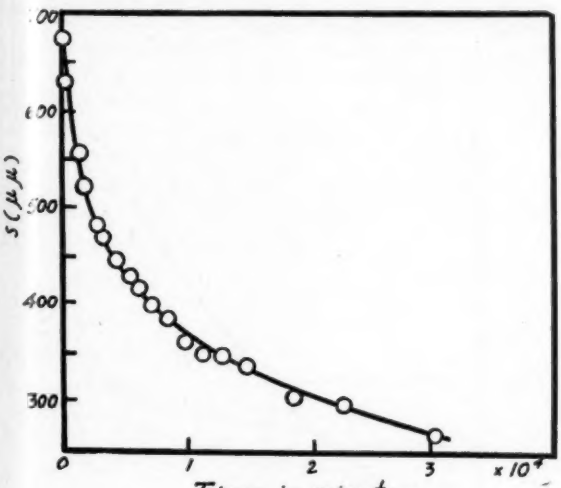


Fig. 7

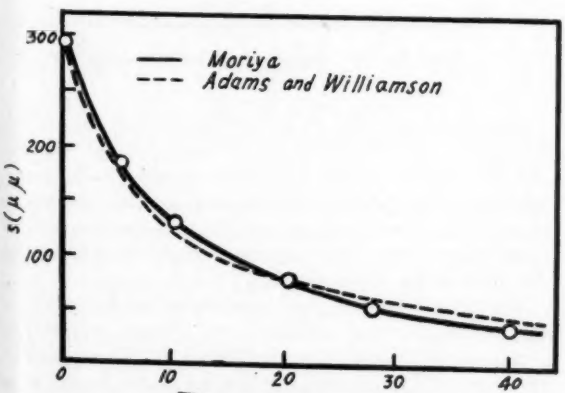


Fig. 8

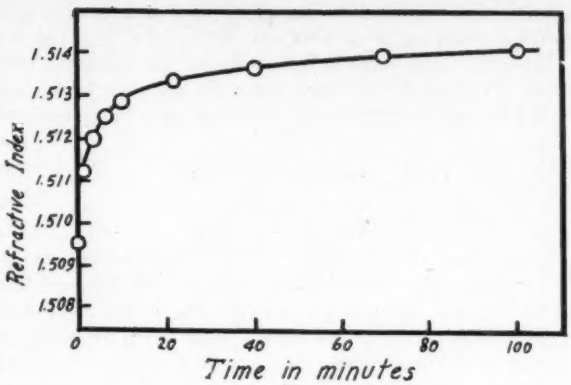


Fig. 9

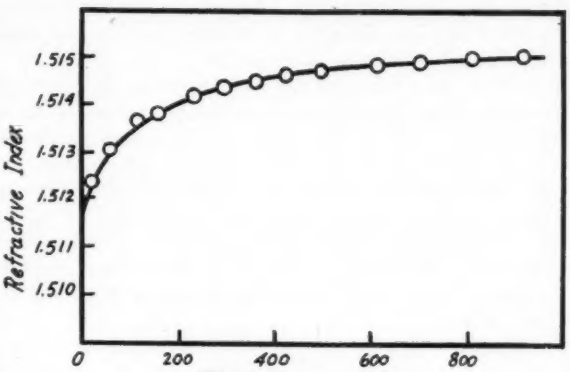


Fig. 10

To illustrate the change of refractive index in annealing range he introduced a new idea which assumes that chemical reactions would take place between the micro-phases being in contact with each other, which lead to formulate a second order rate equation.

Taking into consideration the contribution of both factors, namely, the rate of growth and that of chemical reaction he was able to calculate the rate of change of the refractive index, which was compared with the experimental values of McMaster[13]. The curves in Figs. 9 and 10 show the result obtained.

In short Moriya's theory may be regarded as being characterized by the assumption of the existence of micro-phases in glass, whose rate of growth as well as the rate of chemical reaction play an important role for illustrating the time dependency of some properties of glass in the annealing range.

2. M. Mine's Experimental work

On the relaxation phenomena as mentioned above M. Mine[14] made systematic studies on the change of the density of glass with time in the annealing range. He used glass rods of the composition SiO_2 71, Al_2O_3 2, B_2O_3 1, CaO 6, ZnO 2, K_2O 6, Na_2O 11 percent. The rod was reheated in an electric furnace having a uniform temperature gradiant along its axial direction during a predetermined holding time. It was then cut into pieces and their densities were measured by the sink float method.

A rod subjected to reheating in a temperature gradient covering from 600° to 300°C. for 100 minutes gave the same value at both sides of the maximum density at about 490°C. Such value D_m and the corresponding T_m are the function of time and may be represented as

$$D_m = D_{m\cdot 1} + d \log_{10} t \qquad (10)$$

and

$$T_m = T_{m\cdot 1} - c \log_{10} t \qquad (11)$$

where $D_{m\cdot 1}$, d, $T_{m\cdot 1}$ and c are the constants having, respectively, the values 2.4920 (g/m³), 0.0024 (g/cm³), 527°C, and 18°C in the present case. It was confirmed that these formulae hold good even if the reheating is continued for a month, from which it may be concluded that the temperature giving maximum density decreases, and the corresponding maximum density increases with the increasing holding time which may be extended to number of years. In other words the most compact state of glass is practically unattainable.

On the other hand the densities of intensively quenched samples have shown the increase by reheating at a temperature far below the lower annealing point. A water quenched sample, for example, has proved the increase in density at the third decimal place by heating for an hour at a temperature as low as 100°C. Regardless of quenching conditions the densities of all samples, recovered almost instantaneously to the value of the rod as drawn if they were reheated to the temperatures higher than 400°C.

This basic idea underlying Mine's interpretation of the relaxation phenomena is, essentially, similar to that of Tool[15] so that it will not be necessary to refer to the matter in detail.

3. Thermodynamic Approach of E. Kanai and T. Satoh

At a constant temperature such physical properties of glass as density, refractive index, and viscosity approach a definite value irrespective of previous thermal history. We thus understand tacitly that there exists an equilibrium state corresponding to the temperature, although it will not be a true thermodynamic one but will be a conditional equilibrium. If the time required for stabilizing, viz. the relaxation time, is the order of our daily experience we may observe several irreversible changes taking place during the process of stabilization. Such changes do not occur independently but they are correlated with each other through an intricate mechanism. Tool sought such mechanism in the internal structure and Douglas and Jones represent it by configuration, but E. Kanai and T. Satoh[16] made an attempt to find out the origin in the modes of the internal motion of glass.

For this purpose the mode of internal motion should be considered in detail and they advanced a new idea stating that the internal motion is composed of two principal features, namely, one, the network deformation from one configuration to another and the other the vibrational motion around the instantaneous configuration of the network.

The cardinal difference between these two modes is that the latter exists in the solid as well as in the liquid state, while the former would probably be prohibited as soon as glass solidifies.

In other words the characteristic properties, being usually observed in the transition range, may be looked on as the manifestation of the processes through which the network deformation are prohibited one after the other.

As the quantity representing the modes are separable in accordance with their theory they used the internal energy E of the system putting

$$E = E_{net} + E_{vib} \qquad (12)$$

where E_{net} (p. f_{net}) is the network energy, E_{vib} (T, p, f_{net}) the vibrational energy, and f_{net} in the parenthesis is the partition function of the network.

For E_{vib} and E_{net} they gave the following pictures:

Suppose that at the temperature T the network deformation were suddenly arrested and the whole system were brought to absolute zero leaving, however, the uniform contraction and small vibrations, which would always be under equilibrium with the environment, untouched during the process, then at absolute zero E_{vib} would vanish so that

$$E = E_{net}\ (p,\ f_{net}) \qquad (13)$$

E_{net} may be defined as the potential energy of the system at T less than that being always in equilibrium, while E_{vib} is equal to the sum of this excess potential energy and the kinetic energy.

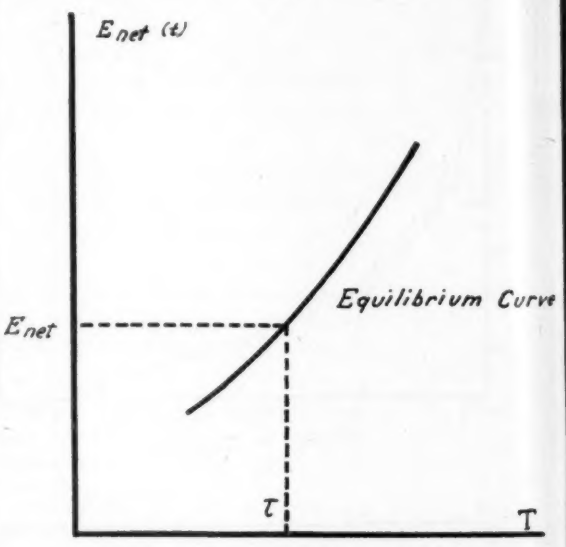


Fig. 11 A way of introducing τ.

Actually E_{net} would be a complicated function of configuration. Taking, however, the analogy with the fact that the vibrational energy may be represented by a temperature scale, Kanai and Satoh proceeded through a short cut by introducing a temperature scale τ, a network temperature, which they assumed, might be able to take the office of the unknown E_{net}.

The meaning of τ was interpreted as the value of E_{net} which it would assume if the thermal equilibrium of the whole system were established. As shown in Fig. 11 τ may be fixed on the equilibrium curve. At the equilibrium τ=T, if the network motion were completely prohibited τ=const, otherwise τ≠T.

In short their theory may be characterized by the proc-

esses for separating and bringing together the constantly dependent factors en masse and representing them by a single term τ, although we have had a vague idea that it represents the initial temperature in the cooling process from which glass begins to lose equilibrium with the environment leaving it in a state corresponding to a higher temperature.

Once the network temperature is defined it is not difficult to formulate the equation of state, or to give the entropy of the system as well as its increment due to vibrational motion.

The network deformation may be regarded as being composed of the motion of a group of several molecules translating step by step through the potential barriers. If we denote the energies before and behind the barrier by E_1 and E_f, the concentrations of the representative systems by C_1 and C_f, respectively, then there exist the relations

$$C_1+C_f=1$$
$$E_1C_1+E_fC_f=E_{net}(\tau) \qquad (14)$$

from which the rate of change of τ may be expressed as

$$d\tau/dt=K(T-\tau) \qquad (15)$$

in which K is the rate constant.

Considering the process of network deformation as being similar to the diffusion phenomena, and assuming that a constant B which expresses the temperature dependency of K is a linear function of τ, the equation (15) may be written as

$$d\tau/dt=A(T-\tau)\ \exp\{(B_1\tau-B_o)/T\} \qquad (16)$$

in which A, B_o, $B_{1\tau}$ are constants.

The results of the calculation were compared with the experimental values obtained by Daragan[17] whose results are illustrated in Figs. 12 and 13.

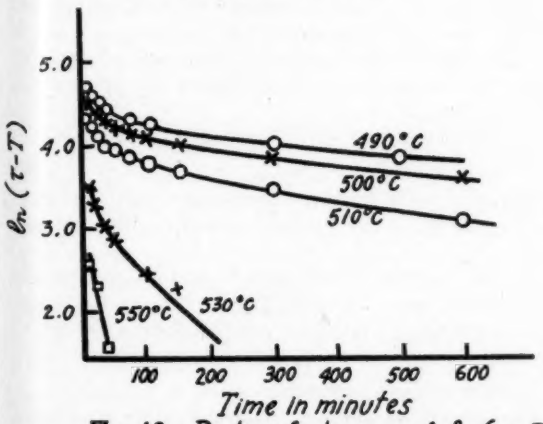


Fig. 12 Rate of change of $\ell_n(\tau-T)$

It will not be surprising if B is not linearly related with τ for intensively quenched glasses. S. Sakka has worked out E-T and E-τ diagrams using the experimental values of the expansion of the glass fiber given by Peychès.[18] The results are shown in Figs. 14 and 15 in which E represents the negative values of B.

In fact we have many evidences which suggest that the flow phenomena may take place at the temperature far below the lower annealing point, namely, as low as few hundred degrees °C. For example: (1) Some glass fibers tend to diminish in length by heating at about 200°C.

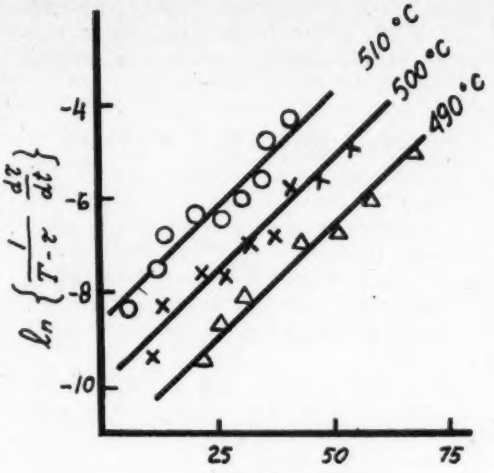


Fig. 13. $\ell_n\left\{\frac{1}{T-\tau}\frac{d\tau}{dt}\right\}$ versus $\tau-T$

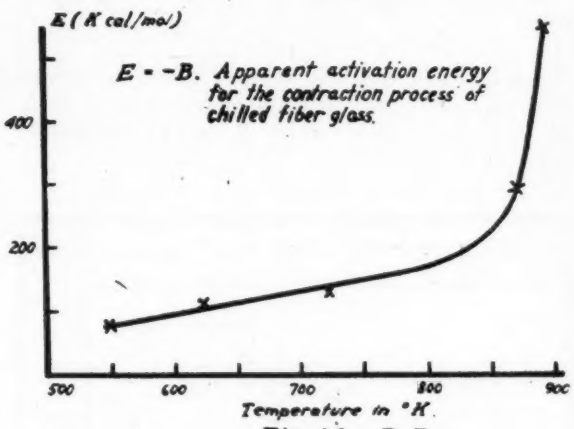


Fig. 14. E-T

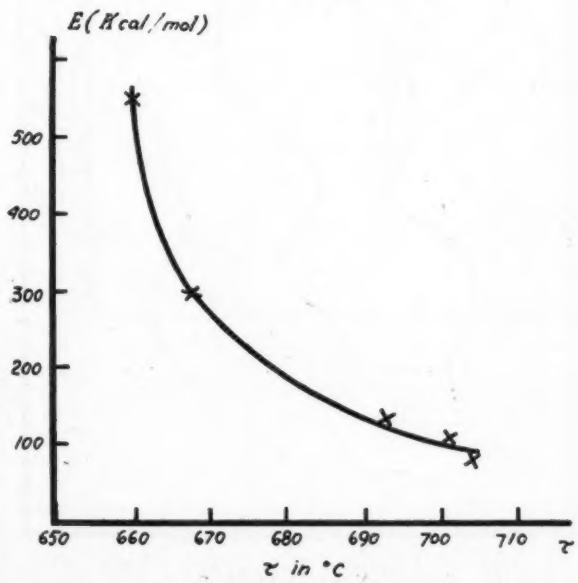


Fig. 15. E-τ diagram

(2) the colorless fibers of copper ruby glass begin to flash at about 250°C. (3) at 300°C. an appreciable amount of Ag^+ ions are able to substitute Na^+ ions by thermal diffusion.[19]

4. Linear Polymer Approach by J. Furukawa

Recently J. Furukawa has presented a paper[20] "On the State of High Polymers." Although he confined his discussion to the behavior of a linear polymer in which only the secondary forces such as van der Waals' forces are forming the pseudo cross-links between the neighboring polar groups he was able to give the interpretation of the characteristic phenomena of the glassy state familiar to glass scientists.

The flow phenomena of glassy high polymers are attributed to momentary separation and reunion of cross links due to thermal and external influences, which bring the relative motion of the chains, composed of an array of chemically bonded atoms.

Fig. 16 is a schematical representation of the system under consideration.

The theory of rubber like elasticity presents an expression

$$s/A=\nu kT(\lambda-\lambda^{-2}) \qquad (17)$$

for the system in which s is the stress exerted on the cross sectional area A, ν the number of cross-links or of chains per cc, λ the elongation ratio of chain, k Boltzmann's constant.

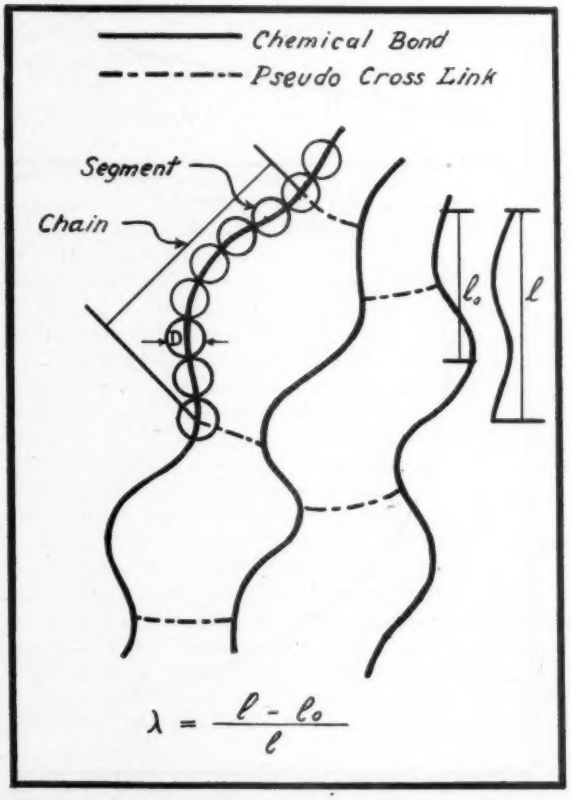


Fig. 16 Schematic Representation of a linear polymer.

In order to apply this equation to the system cross linked by secondary forces the rate of change of ν should be taken into account for which he assumed the relation.

$$d\nu/dt=K_o(N_o-\nu)-K'_o\nu \qquad (18)$$

a monomolecular reversible rate equation with regard to the number of cross links ν and that of unlinked segments $(N_o-\nu)$, may be expressed in terms of the increments of enthalpy and entropy, $\triangle H$ and $\triangle S$, so that

$$\nu/N_o=1/\{1+\exp(-\triangle H/RT+\triangle S/R)\} \qquad (19)$$

In the presence of an external force the chains will be stretched and the activation free energy will be decreased as shown in Fig. 17.

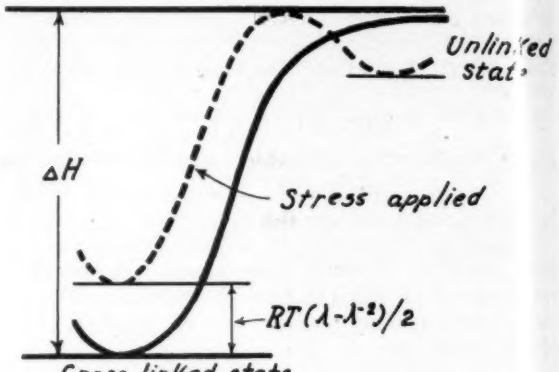


Fig. 17 Energy barriers of natural and stressed state.

With the aid of the equation (19) and taking into account that a segment should have to move to a length equal to half of the diameter of segments before it assumes an activated state the activation free energy may be formulated as

$$\triangle F^*/RT=\triangle H^*/RT-\triangle S^*/R-(\lambda-\lambda^{-2})/2 \qquad (20)$$

Where $\triangle F^*$ is the activation free energy, $\triangle H^*$ and $\triangle S^*$ are increments of enthalpy and entropy in the activated state.

The rate constants under stress Ks and Ks′ are given by

$$Ks=(kT/h)\exp(\lambda-\lambda^{-2})/2\cong K_o e^{-\lambda/2}$$
$$Ks'=(kT/h)\exp\{\triangle H^*/RT+\triangle S^*/R-(\lambda-\lambda^{-2})/2\}\cong K_o' e^{-\lambda/2} \qquad (21)$$

in which h is Plank's constant.

The rate of relaxation of chain elongation at constant cross links offers an expression

$$d\lambda/dt=-Ks'\lambda \qquad (22)$$

The equilibrium concerns both ν and λ, and it is cooperative phenomenon. For simplicity, however, he assigned to the rate of change of cross links the change being by far faster than that of λ so that the latter governs the non Newtonian flow.

The number of cross links ν corresponding to λ can now be written as

$$(\nu/N_o)=1/\{1+\exp(\triangle H/RT+\triangle S/R+\lambda^2\nu/2N_o)\} \qquad (23)$$

The equation (23) does not represent a complete equilibrium, but the disparity from the equilibrium may be

estimated by λ or a fictive temperature τ, which is defined by the equation

$$\lambda^2/2(\nu/N_o)=(\triangle H/R)(1/\tau - 1/T). \quad (24)$$

Since λ tends to approach its equilibrium value, i.e. unity at a constant rate k′ as

$$d\lambda/dt = -k'\lambda \quad (25)$$

from equations (24) and (25) the change of the state can be expressed by the fictive temperature as follows

$$d\tau/dt = -k'(\tau/T)(\tau - T)/2 \quad (26)$$

an expression being similar in form with the well known Tool's equation but containing no arbitrary constant.

By the reversible migration of cross-links along the longitudinal direction viscous flow results. It is necessary, however, the minimum change of cross-links $\triangle\nu$ should be more than constant value b i.e.

$$\triangle\nu = K'_o\triangle t > b \quad (27)$$

or in other words the viscous flow can be observable only when the experimental time scale $\triangle t$ is longer than the relaxation time of separation, i.e. $1/K'_o$. And Furukawa advanced an expression

$$K'_o\triangle t = b \quad (28)$$

as the one which defines the glassy state. Below this point glass behaves as an elastic body.

Using the equation (20) the equation (26) may be transformed into

$$\triangle H^*/RT = \ln(KT/h) + \triangle S^*/R + (\lambda - \lambda^{-2})/2 - \ln\triangle t, \quad (29)$$

and if $\lambda \cong 1$, $\triangle t \cong 1$ sec, this becomes

$$\triangle H^*/T = \triangle S^* + 30R \quad (30)$$

The heat or entropy of activation is likely to be equal to that of formation of cross bond, $\triangle H$ and $\triangle S$, respectively. It can be said

$$\triangle H/T = \triangle S + 30R \quad (31)$$

and at the glassy point the number of cross links is

$$\nu/N = 1/(1+e^{-30}) \quad (32)$$

This means that, at the glassy point, the high polymer is in the iso cross-linked state, and it is also in the iso viscous, iso elastic and iso free volume state.

M. Mine was able to derive Tool's equation assuming that at the temperature τ the ionic distance in glass begins to be arrested, and E. Kanai and T. Satoh introduced the term τ for representing the mode of network deformation, and finally J. Furukawa introduced τ for the purpose of reducing λ to unity.

5. Structure of Borosilicate Glass by T. Abe

T. Abe advanced a new theory on the structure of borosilicate glass[21]

In soda borate glass he suggested the existence of XY_4 group in which X and Y represent, respectively, BO_4 tetrahedron and BO_3 triangle. He considers that B-O bonds in BO_3 tetrahedron which locates in the central part of XY_4 group are very strong, and that this tetrahedron is formed at the expense of loosening of B-O bonds in the BO_3 triangle around it making BO_3 triangles more unstable than those in the normal state.

In borosilicate glass the possibility of the existence of such groups as XY_3Z, XY_2Z_2, and XYZ_3, where Z represents SiO_4 tetrahedron, might be assumed. However, the decrease of stability, being brought out by the replacement of two-dimensional Y by three dimensional Z as well as the liability of segregation, would exclude the possibility of the existence of groups other than XY_4.

When soda content exceeds a certain amount in the Na_2O-B_2O_3-SiO_2 glass Na^+ is supposed to begin to cut the B-O bond of Y surrounding X. It is highly probable that these Na^+ ions would then be trapped into the deep potential holes, which gives rise to the so called "enclosed" Na^+ ions being not so free as those existing in excess. Supposing that one Na^+ may be enclosed for each XY_4 it is concluded that the free Na^+ would first come out in the structure when the Na_2O content exceeds a finite value, namely, 28.6 mol per cent, which indicates the location of maximum transition temperature in the ternary system of Na_2O-B_2O_3-SiO_2.

He attributes the origin of the exsolution, or the separation into two phases, being characteristic especially in borosilicate glasses, to the formation of XY_4 groups which occur by the entrapping of Na^+ ion by BO_4 tetrahedron.

6. Experimental Work of Y. Tamura and Y. Mori on the Exsolution of Borosilicate Glasses.

Even since the invention of Vycor glass the exsolution, or the separation into two phases, of borosilicate glass seems to be continuously attracting the attention of our glass scientists. As early as in 1944 Y. Sakurai[22] carried out an X-ray investigation of the structure of the skeleton being left behind after the soluble part of borosilicate glass was leached out, while Y. Mori found out very recently that this skeleton begins to shrink at about 100°C.

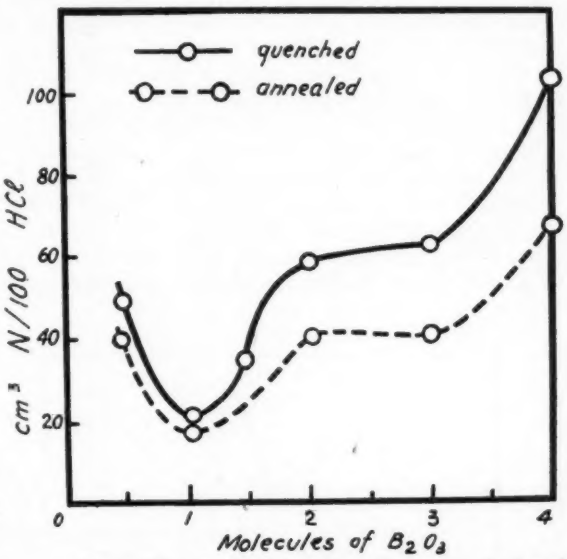


Fig. 18 Solubility of water quenched and slowly cooled glasses $6SiO_2 \cdot B_2O_3 \cdot 2NaO_2$

Y. Tamura[23] compared the water solubility of the quenched and well annealed borosilicate glasses of the molar composition of $6SiO_2 \cdot XB_2O_3 \cdot YNa_2O$, and found that some of them become more soluble by annealing, which is just the reverse trend of ordinary glasses. In Figs. 18 and 19 are shown the solubilities of quenched

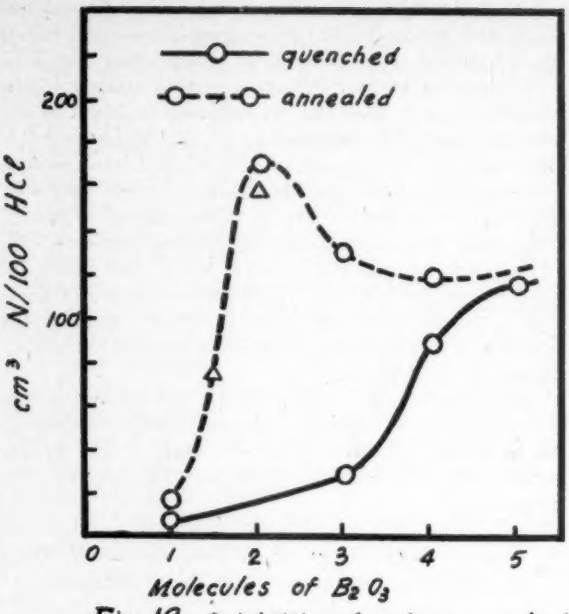


Fig. 19 Solubility of water quenched and slowly cooled glasses. $6SiO_2 . 2B_2O_3 . 0.5Na_2O$.

and well annealed glasses containing different amount of Na_2O.

The cause of this striking effect of annealing was attributed to the exsolution which had taken place in the specimen by holding at moderate temperature which led to the formation of the structure being composed of the more soluble low silicious glass and high silicious skeleton. It is the former which is responsible for the high solubility of annealed glass.

Y. Mori measured the change in length of borosilicate glasses observed when a dilatometric experiment of an unannealed specimen was suspended in the middle of a contraction course in the annealing range and was held at constant temperature. As shown schematically in Fig. 20 the specimen contracts for a while and then begins to expand gradually until the curve runs almost parallel to the time-axis.

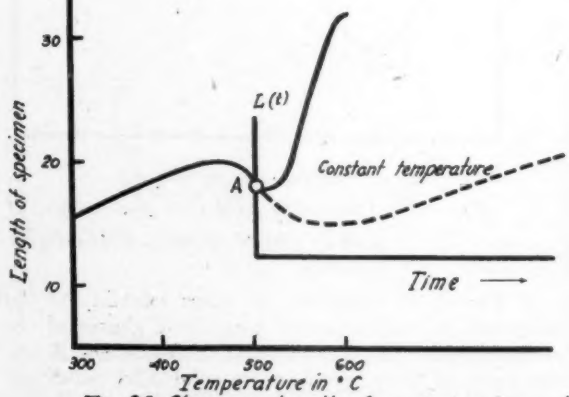


Fig. 20 Change in length of specimen, observed by holding at constant temperature.

According to Mori this characteristic phenomenon may be treated as the superposition of two processes, namely, the contraction and expansion occurring simultaneously. The former would appear as the result of the change in randomness of interionic distances whereas the latter would be the manifestation of the exsolution process.

He proved that the process may be represented by a formula

$$L(t) = l'_o e^{-k't} + l'_o e^{-kt} + L_o(1 - e^{-kt}) + \text{const} \quad (33)$$

If the dilatometric experiment is suspended at comparatively high temperature the first term of the equation will drop out.

Tamura attributes the cause of the volume expansion accompanying the exsolution process to the loosening of the separated (SiO_4) network, which in quenched state is strongly deformed due to attraction towards the high contracting alkali-borate glass.

7. R. Yokota's Work on the Color Center

The decrease of transmission of glasses in ultraviolet and visible region by the irradiation of X-ray or electron beam has long been known as "solarization", leaving, however, the cause unanswered.

R. Yokota[24] may probably be credited as the first to carry out systematic investigations on this problem, pointing to this phenomenon as the outcome of the formation of color centers by X-ray irradiation. His result was recently re-examined by Stevels[25], who also admitted Yokota's theory. As the study of color centers is known to us as a powerful means for investigating the structure of ionic crystals, he may be said to have extended the field of such research to the solids containing the character of homopolar binding, viz. vitreous silica.

The induced absorption bands of the samples of vitreous silica prepared in the oxidizing and in the reducing conditions followed by X-ray irradiation, and the optical and thermal bleaching as shown in Fig. 21 proved the existence of O^{2-} vacancies in the (SiO_4) network in which electrons are trapped. Furthermore, in glasses containing alkali ions, it was revealed that the visible band is due to the electrons trapped by O^{2-} vacancies neighboring alkali ions and that the ultraviolet bands is due to positive holes trapped by alkali ion vacancies

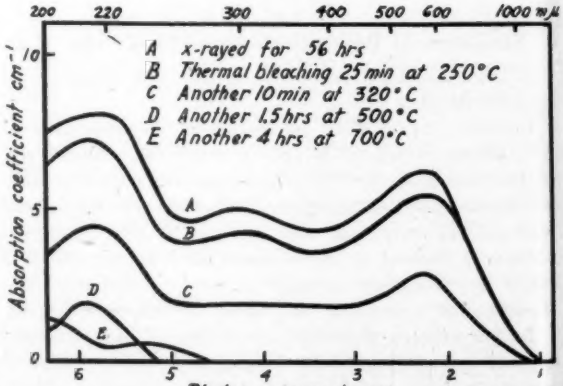


Fig. 21 Induced absorption bands in fused quartz.

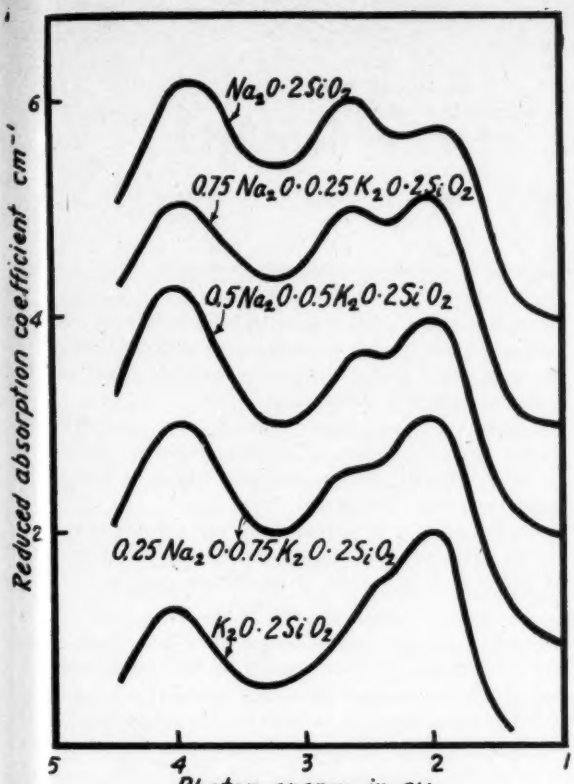


Fig. 22 Induced absorption bands of alkali silicates

neighboring oxygen ions. In Fig. 22 the induced absorption bands of some alkali silicate glasses are reproduced.

As shown in Fig. 23 the substitution of alkali by alkaline earth was found to bring out no appreciable change in the absorption band, while SiO_2-CaO glass gave characteristic figures (Fig. 24). Comparison of the results obtained by the measurement carried out at room temperature and at 90°K, or the absorption in infra red (1μ —5μ) failed to disclose any new absorption band.

As for the influence of substitution of alkali by alkaline earth Yokota gave the following explanations. The substitution of alkali silicate glass gave no characteristic absorption band. According to the X-ray study of Biscoe[26] Ca^{2+} may substitute for Na^+. As Ca^{2+} and Na^+ have about the same ionic radius, the divalent ion Ca^{2+} will be more powerful for tightening the network during the process of solidification of the glass. Ca^{2+} ion draws more unsaturated oxygens than Na^+ for satisfying electric neutrality. As the bond Ca-O is stronger than Na-O the probability of the formation of holes neighboring Ca^{2+} will be by far larger than those neighboring Na^+.

As the field intensity of Ca^{2+} ions is strong enough to form a perfectly coordinated arrangement of O^{2-} ions around them leaving no space for O^{2-} vacancy which traps electrons by X-ray irradiation, the vacancies in the vicinity of Na^+ ion would become the cause of color centers. This is the reason why the introduction of alkaline earth does not bring out the characteristic absorption band. In other words the absorption bands, in these ternary glasses are due entirely to alkaline ions.

8. Yamate and Sakka's Hole Hypothesis of Glass Structure

According to T. Yamate, S. Sakka and the writer the glass structure is characterized by the random distribution of holes of various sizes extending in continuous network. If it is assumed that there is any regularity in their arrangements we are then speaking of crystals, not

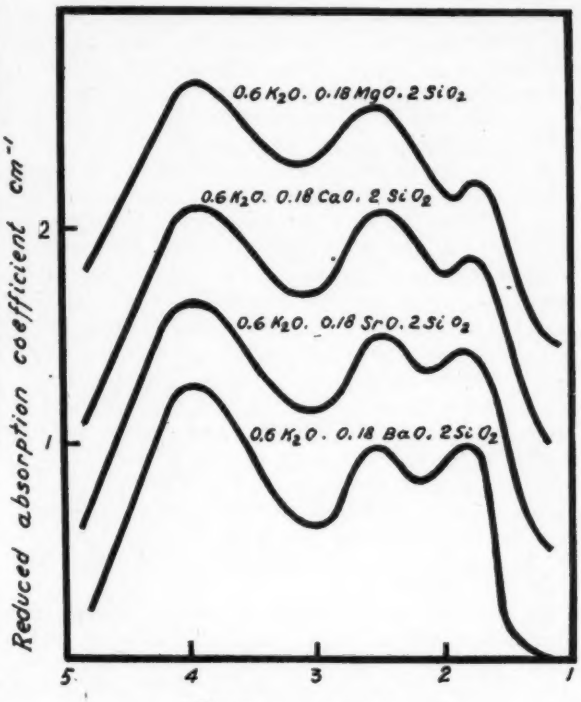


Fig. 23 Induced absorption coefficient of $0.6K_2O \cdot 0.18RO \cdot 2SiO_2$ glass, where R represents Mg, Ca, Sr and Ba respectively.

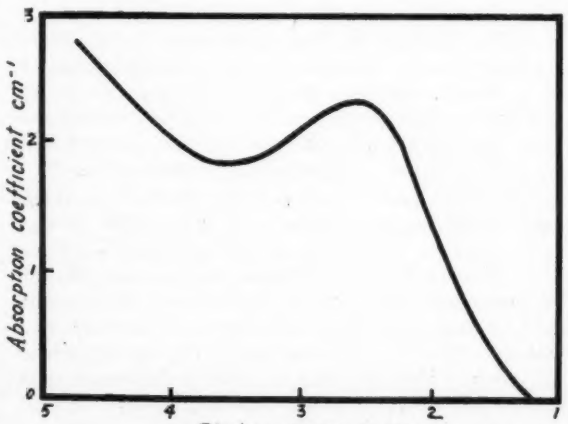


Fig 24. Induced absorption band of $2CaO \cdot 3SiO_2$

Table 3

The variation of the number of holes having two different volumes with the temperature change

Temperature in °K	1000	1200	1400	1600	1800	2000
x_1	2.7	3.8	4.8	5.7	6.6	7.4×10^{22}
x_2	8.6	8.1	7.6	7.2	6.7	6.3 "

glasses. The characteristic properties of glass, therefore, are attributed to the randomness of the spatial distribution and of the size of holes, although both are, as a whole, in statistical equilibrium with the environment.

Selenium crystals are known to be composed of chain molecules running parallel at a definite interval. The difference between the structure of crystalline and glassy selenium may be attributed to the randomness of the spatial distance between the chains being found in the latter, so that the latent heat of fusion, 1.56 Kcal/g atom, may be stored as the surface energy at the points where the spatial distances between the chains deviate from the regular value. The total volume of holes, being pictured as above may be worked out with the result of 3.1 cc at the temperature very near the melting point. If we venture to assume that the energy of 1.56 Kcal/g atom can be stored in glassy selenium as the surface energy at the holes, then its amount referred to unit area will become the order of 10^2 Erg/cm^2, i.e. the surface tension of liquid selenium, when we assign, respectively, the values of the order of 10^{23} and 3 - 4 Å to the number and diameter of the holes which are reduced to spheres.

In oxide glasses we imagine a volume enclosed by oxygen ions whose electron density distribution probability decreases towards its center, and the strains in chemical bonds, which is the outcome of the irregularity of ionic configuration in random network will be in balance with the deformation of the electron clouds towards its center. It would, however, be possible to assume the existence of some larger holes enclosing the atoms of adsorbed gases being bonded chemically at their surface, and a few of them might be so large as the so called Smekal's cracks.

In molten glass the holes migrate from point to point throughout the mass and they amalgamate and dismember at every moment provided the total energy assigned to the holes is constant with regard to temperature. The fact that gaseous oxygen can pass freely through molten glass may be attributed to the migration of the holes carrying adsorbed oxygen atoms on their surface.

As soon as glass begins to freeze the wall of oxygen ions surrounding a hole acts as an increasingly stronger barrier against its movement, because the displacement of a hole may only be possible by the movement of wall-oxygens across the center of the volume, which creates the new holes at another place. It is assumed, however, that the movement of holes as well as their appearance and disappearance continue to occur at the temperatures located well below the lower annealing points.

To the surface energy of a hole is assigned the role of acting as the driving force of the relexation phenomena, but the most characteristic feature of the hypothesis is an attempt to explain the striking contrast of the properties of the differently matured glass usually found by intensive quenching.

For this purpose they ventured to assume that the higher the temperature of molten glass the more will be the holes with smaller diameter which at lower temperatures merge into larger ones.

At this point some explanations are deemed necessary. Let us assume, for simplicity, that (1) the surface energy of a hole is proportional to its surface area, or

$$\xi = a v^{2/3} \phi \qquad (34)$$

where $av^{2/3}$ is the surface area of a hole, and ϕ the surface energy per unit area of a hole, and that 2) the change of surface area due to the amalgamation and dismemberment of holes is by far larger than those due to the change of temperature so that the latter may be neglected, or

$$V = x_1 v_1 + x_2 v_2 + N v_m = V_h + N v_m \qquad (35)$$

where V is the total volume, V_h the total hole volume being pictured as above, N the number of atoms in V, v_m their volume including the regular vacant space, and x_1 and x_2 are the number of holes having the volume v_1 and v_2, respectively.

Confining, for simplicity, attention to two kinds of volume v_1 and v_2 the free energy of the system, F, was worked out, which, by putting $(\partial F/\partial x) = 0$, leads to the expression

$$(1/x)\{x_1(1-a)+\beta+N\}^{1-a}(\beta - a x_1)^a = \exp\{(a\phi/kT) v_1^{2/3}(1-a^{1/3})\} \qquad (36)$$

in which $v_1/v_2 = a (<1)$ and $v_h/v_2 = \beta (>1)$.

Neglecting the volume change of a hole due to temperature change it may be concluded that the right hand side of the equation will become smaller with increasing temperature. And the left hand side will also become smaller with the increasing value of x_1. As x_1, represents the number of smaller holes the above equation states that the higher the temperature of the system is, the more stable if it contains the larger number of smaller holes.

Yamate and Sakka proceeded further to carry out calculations of the order of magnitude under these drastic assumptions, viz., (1) $v_1/v_2 = \tau = 1/2$, (2) the average size of holes is in the same order of that of ions whose total volume amounts to about 10 per cent of the total volume of ions, (3) the average surface energy with regard to temperature is of the order of 40 Kcal/mol. In Table 3 are given the results indicating the trend that the number of smaller holes increases with the increasing temperature.

(*Continued on page* 234)

Optical Society Meets in New York

When glass is subjected to 9000 atmospheres at room temperature, glass properties change after four hours, to the extent that it takes them twelve hours to recover to their original values after the pressure has been released. Optical properties affected were measured by National Bureau of Standards scientists C. Weir, S. Spinner, I. H. Malitson and W. S. Rodney, who reported this interesting finding to the Winter Meeting of the Optical Society of America at the Statler Hotel in New York, March seventh to ninth.

This was the one study of explicit reference to glass formally presented at a meeting which was exemplary in the attractiveness of subjects selected as well as the standards and discipline of presentation, particularly of invited addresses. Transparent materials for light and infrared optics, as well as for new illumination devices were much discussed informally and glass has its ever increasing share.

THE GLASS INDUSTRY found most interesting a symposium of invited papers on luminescence, ably chaired by the Naval Research Laboratory's Dr. J. H. Shulmann. Six prominent speakers, who told of startling inventions in the field of electroluminescense from the wealth of their own experience, did this in a mode of communication that was generally understood, illustrating with perfect slides and completing every message on the minute.

After the theory had been presented by F. E. Williams, General Electric, G. R. Fonda, and C. H. Haake, Westinghouse, B. Kazan, reporting for himself and F. H. Nicoll, both RCA, gave a wonderful survey of applications to come in the fields of light amplification. These "solid state intensifiers" operate by the emission, as a voltage is applied, of light of much greater brightness (and total energy) than the stimulating radiation. The image of an X-ray tube can be made 30 times brighter (Philips). Radar images can be displayed with great visibility. Glass is used as a base for sandwiched layers, one of which may be a photoconductor triggering the electroluminescent effect. These are devices leading to important media of illumination and optics.

The first day of the meeting brought a large array of papers on color, introduced by another series of invited papers in which signal discoveries were revealed and reviewed. It seems, for instance, that the discrepancy between several famous color perception systems can be explained, according to Dean Farnsworth, United States Navy Medical Research Laboratory, New London, when the fact is accounted for that the time for which a blue color is observed in a matching operation greatly affects the sensation of this particular blue. The Munsell Color Company has just completed a new book on color, containing 650 colors of certain hues.

Inter Society Color Council

As is customary, the Optical Society Meeting was preceded by the convention of the congenial group known as the Inter Society Color Council, March fifth and sixth. This group now has, we believe, more than 25 scientific societies which coordinate and enjoy discussion on color questions.

The center of attention, illustrated by a colormad exhibit of *House and Garden* and an address by color stylist G. J. Pollard, General Motors, was on color trends in fashion. This reviewer finds it unfortunate that the account, as did Dr. Kinsey's famous monologue, states what is being done, rather than discussing motivation and animation—and therefore finds that he cannot take their predictions seriously. At any rate, on the surface, people are apparently continuing to hold lilacs in low esteem, are in the depth of a trend away from white and light colors, and increasingly fond of greys, greyish mixes and dark colors, particularly greens. These trend analyses admittedly include trims and sheds. The architects were chided for color unawareness and those present pleaded guilty for those absent. The level of discussion was high, and instructive for those who are sensitive to color in our world and in our industry. The Council deserves our acclamation.

AMERICAN POTASH & CHEMICAL ENLARGES RESEARCH LABORATORY

A $200,000 addition to American Potash & Chemical Corporation's Whittier (Calif.) research laboratory was opened recently as part of the company's expanding research program.

The new addition, which doubles previous workroom space, consists of three four-man labs, two three-man labs, a small lab for micro-analytical work, two large labs for process development, other rooms for allied uses.

With expanding research activities, personnel at the company's Whittier facility has more than doubled since the lab was opened three years ago. With less than 30 employees in 1953, the lab now has a staff of 65 under the direction of Dr. William Emerson.

Joseph C. Schumacher, AP&CC vice president in charge of Research, acted as host for the affair. He introduced Peter Colefax, company president, as main speaker for the event.

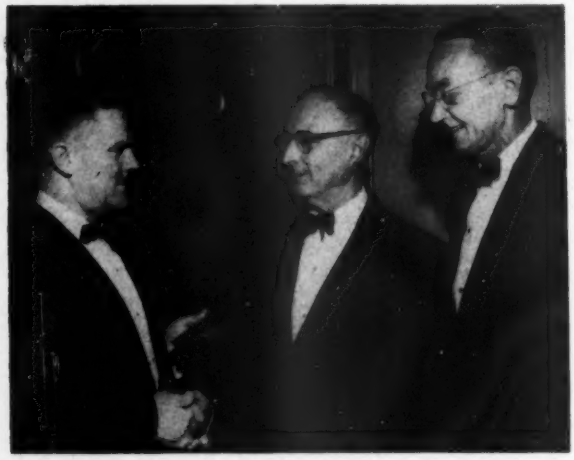
In his talk, Colefax pointed out that American Potash & Chemical Corporation has tripled its research budget and investment in research facilities in recent years.

Important research programs conducted by the company, according to Colefax, have been in connection with lithium carbonate, lithium hydroxide, boric oxide, elemental boron, borate esters, phosphoroborine compounds, parathion, various electrochemicals and others.

FRANCIS C. FLINT RECEIVES BLEININGER AWARD

On March 15, 1957 the Pittsburgh Section of the American Ceramic Society held its annual banquet in the Terrace Room of the Penn-Sheraton Hotel to present the Albert Victor Bleininger Memorial Award to Mr. Francis C. Flint, Technical Director of Hazel-Atlas, Division of the Continental Can Company.

The two hundred and forty-two members and guests were welcomed by Dr. Edwin Ruh, Secretary of the Pittsburgh Section, who, next, introduced Dr. E. F. Osborn, Dean of the School of Mineral Industries at Pennsylvania State University, as the Toastmaster for the evening.



Francis C. Flint receives the Albert Victor Bleininger Award bronze medal from C. Burton Clark, Chairman of the Pittsburgh Section, American Ceramics Society. At right is C. L. Thompson, Chairman of the 1957 Bleininger Award Committee.

The fast moving program prepared by the Program Chairman, J. Earl Frazier, was opened by Karl Schwartzwalder, President of the American Ceramic Society, who told of the purpose of the Bleininger Award. Dr. J. T. Littleton, Vice President Emeritus of Corning Glass Company, the speaker of the evening, told about Francis Flint. The incidents of his boyhood and early college days, provided by Dr. John Hostetter, former medalist, served as a prologue to the incidents recalled by Dr. Littleton during his association with Mr. Flint as they worked together developing the Glass Division of the American Ceramic Society.

Mr. Flint was greeted by a standing ovation as he was presented to the audience by Dr. C. L. Thompson, Chairman of the 1957 Bleininger Award Committee.

Mr. C. Burton Clark, Chairman of the Pittsburgh Section, presented Mr. Flint with the bronze medal and the scroll symbolizing the award in recognition of his services and contributions to the ceramic industry in Europe as well as in the United States.

After a few words of acceptance of his newest honor, Mr. and Mrs. Flint had an opportunity to accept the congratulations of their friends at an informal gathering in the Flint Hospitality Room.

GLASS BOTTLE BLOWERS HOLD CONVENTION

A prediction that America's glass industry would achieve still higher production and greater prosperity was made during the 61st convention of the Glass Bottle Blowers Association, AFL-CIO, held in St. Louis March fourth through eleventh. The convention of the 115-year-old union was attended by 630 delegates representing the union's 52,500 members in the United States, Canada and Puerto Rico.

Reelected to the international presidency of the union was Lee W. Minton, 45, who has headed the G.B.B.A. since 1946. Also reelected were Raymond H. Dalton, vice-president since 1949; Newton W. Black, secretary since 1949; and Howard A. Taylor, treasurer since 1955.

A number of the nation's leading glass firms participated in the convention activities by setting up special exhibits which were open to the delegates and the St. Louis public. Among the industry's exhibitors were Owens-Illinois whose working model of a glass furnace attracted thousands, Hazel-Atlas Divison of Continental Can Co., Ball Brothers, Kimble Glass Co., L.O.F. Glass Fibers and Owens-Corning Fiberglas.

A deeply-mourned casualty of the exhibit was the largest hand-blown glass bottle in the world which was broken in transit before arrival. This container, which was being lent by the Armstrong Cork Company, was manufactured in 1906 and had a capacity of 70 gallons.

The convention gave unanimous approval to a resolution commending the Glass Container Manufacturers Institute for its advertising campaign in magazines, trade publications and in the labor press. It urged continuation and expansion of this campaign to achieve maximum results in increased sales which will be of mutual benefit to both the union's members and to the industry as a whole.

The dominant union in the glass field, G.B.B.A. lists among its membership all but a fraction of a percentage point of the workers in the glass container industry and a constantly increasing majority of fiber glass workers. Mr. Minton reported to delegates on the efforts to amalgamate with other glass unions in North America. These include the American Flint Glass Workers Union, United Glass and Ceramic Workers and the Window Glass Cutters League. A merger between the G.B.B.A. and the U.G.C.W. appears most likely in the near future, though officials of the other two unions are also interested. Mr. Minton predicted, however, that eventual amalgamation of all four unions was inevitable and that there would ultimately be a single glass workers union with membership of 150,000.

A group of G.B.B.A. members will leave in July for England to study that country's glass industry, while a similar group of British glass workers comes to this country. Mr. Minton expressed the belief that no other union has ever adopted a program of this type without governmental payment of costs involved. Expenses for the American team will be borne by the British union following the delegation's arrival in that country, while G.B.B.A. will assume all expenses of the British team during its six-weeks stay in the United States.

(*Continued on page* 224)

Contributions of Electric Melting and Boosting to Glass Technology

LaBurthe, Borel and De Piolenc in the January 1957 issue of the Bulletin of the American Ceramic Society describe work done and results obtained through the use of electric power in melting, fining, and conditioning glass, either alone or in combination with conventional fuels.

The electrical conductivity of glass is determined by its structure; only the metal ions contribute to its conductivity. The conductivity therefore will be a function of the concentration in metallic ions and of their mobility; the mobility, in turn, is a function of the molecular diameters and of the viscosity of the medium.

For practical purposes, it can be assumed that only the smallest ions, sodium and potassium, contribute to conductivity; this is substantially true for glasses having over 12% Na_2O.

Knowing what ions are involved and their concentration, it therefore is possible to determine the conductivity of a given glass at various temperatures. The actual practice is generally to take resistivity which is of course the reciprocal of conductivity.

Generally speaking, for a known glass where the total of the Na_2O content plus half of the K_2O content varies within small proportions and where the other elements do not appreciably influence the viscosity, it can be said that the resistivity is a linear function of the Na_2O and K_2O content.

Resistivity of a glass can be derived from that of a known glass by the formula: $pm = pn \times n/m$ where m and n are the soda equivalent contents of the two glasses.

For glasses that are very different in composition, it is safer to actually measure the resistivity in the laboratory.

The amount of heat required to melt the batch materials and cullet and take care of chemical reactions between constituents varies according to the composition and temperature at which the glass is used, but is in the vicinity of 270 watt-hour/lb. of molten glass using 30% cullet.

The heat loss through the walls of electric tanks varies according to size and production rate. It can be as low as 400 watt-hour/lb. in large tanks operating at the rate of 10 sq. ft./ton/day and as high as 1.8 kwh./lb. in small tanks with high production rates.

For the sake of comparison only, a 270 sq. ft. area tank usually will produce 33 tons/day of glass window glass quality with a maximum power of 2500 kw. The specific input is therefore 910 watt-hour/lb. and the average energy input rate in the tank is in the vicinity of 2.8 kw./cu. ft.

It is possible to use a higher rate, particularly to heat small tanks, but there is obviously a limit at which reboil occurs and foaming can reach the point where it completely shuts down production.

When energy is applied only to a zone of a tank, the maximum rate of application is determined by:

(a) how advanced the glass is in its fining process at the point where heat is applied.

(b) the ease with which thermal exchange can take place between the heated zone and surrounding areas, which means particularly the color and thermal conductivity of the glass.

(c) the ability of the glass to be renewed by convection in the heated zone.

It is therefore easy to realize that the location of the zone of energy application within the tank, its shape, its orientation together with the location, shape and orientation of the electrodes will be most important in creating this convection and therefore will determine the maximum energy input rate that the glass will tolerate.

The very fact that the electrical conductivity of glass is ionic in nature precludes the use of power in the form of direct current; only AC can be used, usually at the normally available 50 or 60 cycles frequency. However, if the power is to be generated for the purpose there can be some advantage in using a higher frequency. When DC was used, electrolysis of the glass took place.

In an unlimited body, the power lines between electrodes tend to fill the whole space open to them. The current density per unit cross-sectional area in the glass will therefore vary considerably according to whether the element of cross-sectional area considered is in a zone where the power distribution lines are restricted or, on the contrary, allowed to expand.

Usually the area of maximum restriction will be in contact with the surface of the electrodes and the degree of restriction will increase as the submerged perimeter of the electrodes is decreased in relation to the distance between the electrodes.

Four materials are currently in use and selected according to both their conductivity and heat resistance: Iron, Graphite, Molybdenum and Platinum. The first three materials are easily oxidized at high temperatures; the last one is not.

On the other hand, as materials increase in cost, every effort is made to reduce their weight. Therefore the electrodes usually found in the tanks are: either iron electrodes of very large size consisting of blocks weighing several hundred pounds; or graphite electrodes weighing several dozen pounds; or metal electrodes other than iron either solid (e.g. molybdenum), or liquid (e.g. tin), weighing a few pounds; and finally, but rarely so far, platinum electrodes weighing a few ounces and used for special purposes.

Such a difference in scale necessarily results in a difference in the submerged area of the different types of electrodes and in most cases a difference in the current density at the surface.

The figures which follow should not be considered as absolute, but in most cases it will be found that: (1) Iron electrodes apply current to the glass at a maximum rate of 2 amp. per square inch of submerged area; (2) Graphite electrodes apply current to the glass at a maximum rate of 6 amp. per square inch; (3) Molybdenum electrodes apply current to the glass at a maximum

rate of 20 amp. per square inch; (4) No figures will be mentioned for platinum electrodes because they have not been used very extensively, mostly for conditioning jobs which do not compare with production tanks.

Electric tanks can be divided into three classes from the standpoint of electrode arrangement.

(1) Those in which large electrodes located opposite one another apply current at right angles to the glass flow. The glass in the vicinity of the electrode reaches a substantially similar temperature to that in the center of the tank and convection in this case is seldom enough to create homogeneity.

(2) Those in which electrodes in the shape of bars are located in a horizontal plane close to the surface, at right angles to the flow of glass, and with current flowing in the direction of the flow of glass.

Current is distributed to the glass from the lateral surface of the electrode; in this manner, the same thermal treatment is applied to the glass all the way across the tank.

Furthermore, these electrodes are located very close to the surface and therefore they create a physical barrier to the batch materials floating on the surface. Moreover, the energy concentration around the electrodes, calculated not to reach the critical energy concentration previously mentioned, creates a convection barrier.

The convection currents so created help to homogenize the glass, again, uniformly across the tank.

(3) Those in which the electrodes are located vertically through the bottom of the tank at a distance from the side walls and power is applied within a limited portion of the volume of glass contained in the melting area.

The first type tends to create over the whole area of molten glass a rate of energy dispersion substantially uniform per unit of volume.

The second type provides the glass as it flows with a rate of energy per unit of volume which varies cyclically between a maximum located in the vicinity of the electrodes and a minimum located between the electrodes. This type maintains also a gradient of energy between the surface and the bottom of the tank.

The third type maintains a permanent temperature differential between the zone of application and the surrounding areas.

Electricity has been used to melt glass generally without any major change in the conventional shape of the tanks. However, the flexibility of electric melting makes it possible to use quite unusual shapes. For instance, tanks of hexagonal shape are in operation either as day tanks or as continuous tanks. Other tanks were used experimentally which consisted of a sort of cubilot melting by electricity supplying separate fining tanks conventionally fired.

Most inventors and users have tried to apply electric boosting to fuel-fired tanks by applying power within glass which is being melted by flames. The method appears attractive because heat loss through radiation is substantially paid for in conventional fuel so that electrical energy can be almost completely used to speed up melting and fining of the glass. Actual results, however, are not as good as would be expected from a casual examination. A simple calculation will show why.

Assume that a 540 sq. ft. tank produces 110 tons of flint glass per day. We can assume a specific heat input of 2000 kCal/kg. of molten glass which is not a particularly low figure. The additional glass that can be provided by electrical means requires, as shown above, 270 watt-hours/lb. or 515 kCal/kg. The additional glass will cost the same as the regular glass if 515 electrical calories cost as much as 2000 kCal of the conventional fuel. More briefly, when 1 electrical B.t.u. costs more than 4 B.t.u.'s of conventional fuel, the cost is higher and that, unfortunately, is usually the case.

The operation can still be justified on a temporary basis if, on one hand, the refractory cost per ton of glass is not increased and if, on the other hand, the additional melting cost is offset by an advantage resulting from a temporary economic situation.

CORNING TO EXPAND IN REFRACTORIES FIELD

Corning Glass Works will further expand its activities in the refractories field because of important discoveries made recently in the fields of low expansion and corrosion resistant refractories, according to William C. Decker, company president. Dr. Charles F. DeVoe, formerly director of manufacturing staffs, has been appointed director of ceramic research. Arthur W. Weber, director of engineering, will assume additional manufacturing staff duties in his new appointment as director of engineering and manufacturing staffs.

The move follows only by a year establishment of the company's refractories division which was organized to consolidate the development, manufacture and sale of refractory products. Headquarters for the new ceramic research laboratories will be located in the company's Corning, N. Y. Pilot Plant 2. The group will centralize all ceramic research of the company.

Dr. DeVoe joined the company in 1936 as a physicist and shortly thereafter became engaged in a program which led to development of a method to melt optical glass continuously. He was appointed manager of Pilot Plant 1 in 1948, manager of Pilot Plant 2 in 1952 and the following year was named chief process engineer in the Manufacturing and engineering division. He has been director of manufacturing staffs since 1954.

Mr. Weber became associated with the company in 1935 as a research engineer, serving successively in company plants at Corning, Charleroi, Pa. and Central Falls, R. I. until 1939 when he was named assistant plant manager of the Wellsboro, Pa. plant. He became assistant to the general manager of the Charleroi plant in 1941, plant manager in 1942, and was named manager of manufacturing for the consumer products division in 1945. From 1947 to 1954 he served as chief mechanical engineer until appointment as director of engineering.

• Edward P. Vincent has been appointed glass industry specialist for the Kaiser Chemicals division of Kaiser Aluminum & Chemical Sales, Inc., it was announced by Russel T. Drennan, general sales manager for the divison. Mr. Vincent was formerly at the Creighton plant of the Pittsburgh Plate Glass Company. In his new position with Kaiser Chemicals, he will specialize in refractory service to the glass industry.

Inventions and Inventors

Feeding and Forming

Continuous Production of Flashed Glass. Patent No. 2,751,714. Filed January 21, 1952. Issued June 26, 1956. Two pages of drawings; none reproduced. Assigned to Glaceries de St. Roch Societé Anonyme by Albert Kneff.

The present invention relates to a process and to apparatus for the continuous production of flashed glass, which are applicable to plants for the production of sheet glass both by rolling and by drawing.

In accordance with the invention, the molten base glass is passed under a float constituting a receptacle into which the flashing glass is introduced; also in the molten state, the flashing glass is made to overflow so that it forms on the surface of a base glass in a thin layer which becomes welded thereto, before the formation of the sheet. The thickness of the flashing layer may be adjusted at any time by varying the quantity of flashing glass introduced into the float and the constancy of the thickness of the flashing layer over the entire width of the sheet can be readily maintained, even when this thickness is reduced to a fraction of a millimeter.

The apparatus employed for carrying out the process comprises a trough-like float immersed in the bath of base glass and fed by a small auxiliary tank containing the flashing bath. For the manufacture of flashed glasses of different colors, a number of auxiliary tanks may advantageously be provided which, in the inoperative position, are heated by the gases for the heating of the main tank containing the base glass, the auxiliary tank in operation being brought opposite the receptacle which it is to feed.

There were ten claims and the following references were cited in this patent: 1,670,247, Ferngren, May 15, 1928; 1,910,759, Engels, May 23, 1933; 2,264,245, Lytle, Nov. 25, 1941; 576,340, Germany, Sept. 27, 1931 and 584,015, Germany, Sept. 13, 1933.

Glass Rolling Machines. Patent No. 2,760,309. Filed May 11, 1954. Issued August 28, 1956. One page drawing; none reproduced. Assigned to Les Glaceries de la Sambre, Societe Anonyme, by Edmond Laverdisse.

In accordance with the invention, the bulge of a deformed roll is rectified, that is to say, the roll is straightened. This is accomplished without interrupting the rolling of the glass by varying the relative times of contact of the bulge, and of the arched portion of the roll with the hot glass, by an appropriate variation of the speed of rotation of the roll in the course of its revolution. Therefore, the bulge of the roll remains in contact with the hot glass for a shorter time than the arch. Thus, the bulge becomes less heated than the arch and the roll is straightened, owing to the differences in the expansion of its opposite sides.

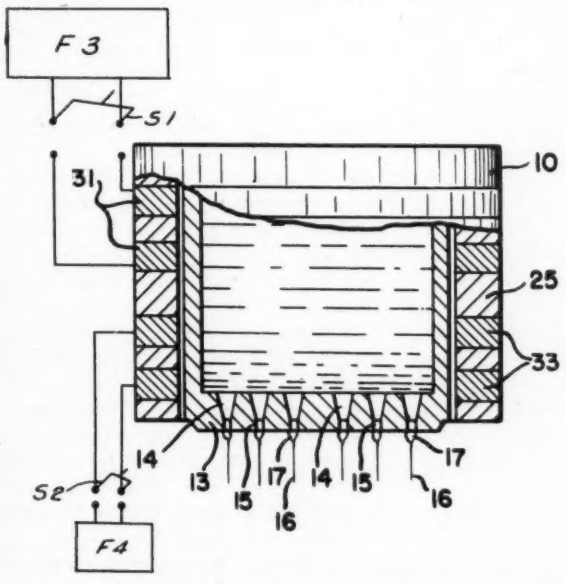
The periodical variation of the speed of the roll to be straightened may be obtained in various ways by acting on the driving mechanism by which it is rotated. If the drive is effected by an electric motor, a simple means consists in periodically inserting in the circuit of the motor, with the aid of a contact, controlled by a cam turning with the roll, a resistance for increasing the speed of the motor during the passage of the bulge of the roll, over the glass, or conversely in short-circuiting the resistance during the passage of the arch of the roll over the glass in order to reduce the speed of the motor while the bulge of the roll is not in contact with the glass.

The cam turning with the roll is advantageously angularly adjustable to bring the boss thereof into coincidence with the most deformed generatrix of the roll, and axially in relation to the member which it actuates in order to vary the duration of the actuation of the contact by which the speed of the motor driving the roll is varied. It is thus possible to adjust the variation of the speed of the roll as a function of the deformation to be corrected.

There were 10 claims and the following references cited in this patent. 1,605,051, Menzies, Nov. 2, 1926; 1,705,672, Menzies, Mar. 19, 1929; 1,728,633, Schmidt, Sept. 17, 1929; 2,627,593, Tietig, Feb. 3, 1953 and 2,691,851, Davison et al., Oct. 19, 1954.

Furnaces

High Frequency Preparation of Molten Glass. Fig. 1. Patent No. 2,747,006. Filed June 23, 1953. Issued May 22, 1956. One page drawings. Assigned to L. O. F. Glass Fibers Company by Randolph H. Barnard.



This invention relates to the heating and melting of glass and more particularly to the production of molten glass of uniform characteristics for drawing into fine filaments.

As shown in Fig. 1, the pot may be surrounded with two coils 31 and 33, one of which receives the energy in the kilocycle range that is 250-300 kilocycles, while the other is supplied with energy in the megacycle range that is, for example, 100 megacycles. Thus, as shown in Fig. 1, the source F3 may provide 250-300 kilocycles to coil 31, while source F4 provides 100 megacycles to the lower coil 33; switches indicated at S1 and S2 are operable to connect the sources and coils as indicated. Such coils may function together or alternately. However, it is necessary to insure that in the former case, the two coils operate at frequencies for the prevalent conditions which do not result in deleterious actions between the fields. Under the conditions stated the molten glass within the chamber would be extremely uniform, for the pot itself, due to the use of the coil, has no hot spots, conductivity from the wall is high, and the energization due to the induced currents within the glass occasions uniformity centrally of the pot or chamber.

The process of invention is particularly useful with glasses which are to be formed into filaments, for such glasses are normally melted around 1800-2000°F. and the specific resistance of the glass in ohms per centimeter per centimeter squared drops rapidly as the temperature increases; thus at about 1300°F. the specific electrical resistance with soda glass is about 100 ohms per centimeter per centimeter squared, while for hard alkali-free glass the specific resistance is somewhat higher and decreases to about 100 ohms per centimeter per centimeter squared at temperatures slightly above 2000°F. Accordingly, the resistance across a 5 inch pot will be quite small when the glass is at a high temperature, in fact only a few ohms, and accordingly induced currents may readily flow.

The filaments drawn in accordance with the invention will exhibit extreme uniformity of diameter and find particular utility in the production of blown fibers, textile yarns and fabrics.

There were 14 claims and 10 references cited in this patent.

Glass Melting Furnace. Patent No. 2,754,346. Filed August 8, 1952. Issued July 10, 1956. One page drawings; none reproduced. Steele D. Williams.

This invention relates to electric furnaces for melting glass batch material and for refining the resultant glass.

The furnace includes a refractory tubular member formed of materials such as silicon carbide, which is capable of conducting electricity but which, in doing so, serves as a high resistance heating element. The interior of the tubular member constitutes the melting and refining chamber of the furnace. The tubular member is closed at each end by a refractory plug and is provided with a protective coating on its inner and outer surfaces. Heating current is delivered to the member by spaced electrodes, each of which is shown in the form of an encircling band, surrounding and in electrical contact with the tubular member. One electrode is shown located at one end of the member and the other is located at the other end thereof. Heating current is delivered to the tubular member through the two electrodes.

The tubular member is inclined to the horizontal and a batch delivery conduit is located adjacent to its elevated end and is arranged to deliver batch forming material to the interior thereof. A glass discharge conduit is located adjacent the lower end of the tubular member and on the lower side. It communicates with the interior of the member and terminates in a discharge orifice which, during a glass melting operation, is normally submerged by molten glass.

In order to prevent caking of batch material delivered to the melting chamber of the furnace, the delivery conduit is cooled. This is accomplished by a cooling coil. For the purpose of supplementing the heat resulting from the delivery of heating current to the tubular member, an induction coil is employed which surrounds the tubular member adjacent the discharge conduit. A second induction coil surrounding the discharge conduit is employed for delivering heat to molten glass leaving the tubular member and moving toward the glass delivery orifice.

There were 8 claims and 21 references cited in this patent.

Forming Fibers. Patent No. 2,754,541. Filed July 5, 1951. Issued July 17, 1956. One page drawings; none reproduced. Assigned to Owens-Corning Fiberglas Corp. by Charles J. Stalego.

This invention relates to method and apparatus for forming comparatively fine fibers from heat softenable material and more especially to the production of fine fibers attenuated from molten glass and the like.

The invention embraces a method of minimizing the existence of unequal pressure or substantially equalizing the pressure adjacent to the primary filaments so as to eliminate the tendency of the heat softened filament being attenuated to fibers to move out of the locus of the attenuating forces. The fibers are attenuated from thermofusible fiber forming material by a blast of gas wherein a reduced pressure or partial vacuum existent at one side of the primary filament of fiber forming material is counteracted, offset or negated in a manner whereby the locus of movement of the fibers during the attenuation operations is substantially in the core of the gas stream of the blast.

The net effect is to prevent the fibers from rolling or coiling up into pellets or slugs and thus disrupt fiber formation.

There were 19 claims and the following references were cited in this patent: 2,489,243, Stalego, Nov. 22, 1949; 2,515,738, Slayter et al., July 18, 1950 and 2,578,101, Stalego, Dec. 11, 1951.

Glass Compositions

Metal Sealing Glass and Seal. Patent No. 2,743,553. Filed November 26, 1951. Issued May 1, 1956. One drawing; not reproduced. Assigned to Corning Glass Works by Wm. H. Armistead.

This invention relates to glass compositions which are suitable for making fusion seals with alloys or iron comprising essentially nickel, cobalt and iron, such as "Kovar" (29 parts nickel, 17 parts cobalt, 0.3 part manganese and 53.7 parts iron) and "Fernico" (28 parts nickel, 18 parts cobalt and 54 parts iron). Such seals are particularly intended for use in the manufacture of electronic discharge tubes such as power tubes, image orthicon tubes, iconoscope tubes, and the like.

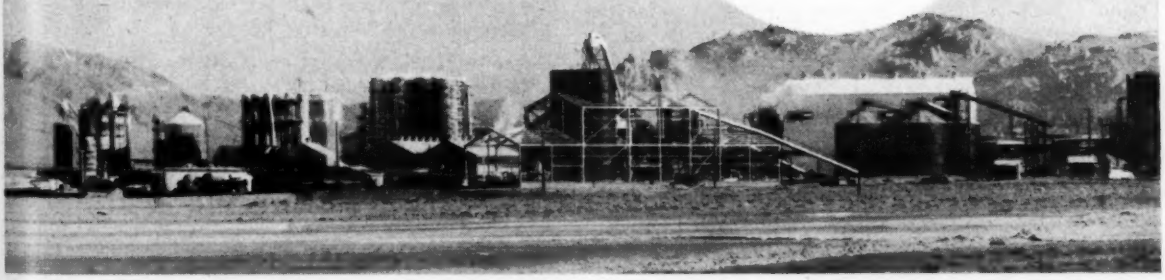
The following compositions calculated in weight per cent from their respective batches illustrate better glasses:

West End anhydrous **SODIUM SULFATE** merits your confidence for its consistent purity

Here is the new high standard of sodium sulfate quality achieved by exclusive West End production techniques and controls. The product is pure white and exceedingly low in heavy metal content. It is guaranteed 99½% minimum Na_2SO_4 yet actually runs 99.75% to 99.8% Na_2SO_4 typically. We invite your attention to the adjacent typical analysis and welcome your communication.

TYPICAL ANALYSIS

Na_2SO_4	99.5% or better
Na_2O	.05% max.
B_2O_3	.05% max.
NaCl	.07% max.
Insoluble	Trace
Loss on ignition	Less than 0.1%
Solution	Clear
Color	White
Fe	1 ppm
As	1½ ppm
Cu & Zn	Not detectable



WEST END

West End Chemical Company

DIVISION OF STAUFFER CHEMICAL COMPANY

EXECUTIVE OFFICES, 1956 WEBSTER, OAKLAND 12, CALIF. • PLANT, WESTEND, CALIF.

SODA ASH • BORAX • SODIUM SULFATE • SALT CAKE • HYDRATED LIME

	1	2	3	4	5	6	7	8	9
SiO_2	70.4	70.4	68.5	69.9	70.25	69.35	68.25	74.25	66.5
B_2O_3	20.1	18.1	20.25	18.1	18	18	18	15	22
Al_2O_3	2	4	3	3	3	3.15	3	1	2
K_2O	7.25	6.5	7.5	6.25	6.5	8.25	10	9	9
Na_2O	....	....	....	2	1	0.5	....	....	....
Li_2O	0.25	1	0.75	0.75	1.25	0.75	0.75	0.75	0.50

As a fining agent approximately 0.5 per cent As_2O_3 may be included in each of the above compositions; substantial amounts of this will be lost during melting; the residue has substantially no effect upon the physical and chemical properties of the glass.

The improved chemical durability of the present glasses when heat-treated is due to their relatively high K_2O content.

The presence of more than 4 per cent Al_2O_3 in the glasses of this invention objectionably increases the melting temperature. At least 1 per cent of Al_2O_3 is required, however, for adequate normal chemical durability.

The electrical resistivity of the glasses of this invention measured at 350°C. ranges from 30 to 500 megohm-cm. Such high resistivities are due to the high K_2O and low Na_2O contents of the glasses.

At least 0.2 per cent Li_2O is essential in the present glasses to maintain easy meltability.

There were 8 claims and the following references were cited in this patent: 2,219,573, Fraenckel, Oct. 29, 1940; 2,279,831, Lempert et al., Apr. 14, 1942; 2,392,314, Dalton, Jan. 8, 1946, and 2,570,020, Armistead, Oct. 2, 1951.

Glass Wool and Fiber

Producing Fibrous Products. Patent No. 2,751,962. Filed November 16, 1950. Issued June 26, 1956. One page drawings; none reproduced. Assigned to Owens-Corning Fiberglas Corp. by Warren W. Drummond.

An object of the invention is the provision of a method of economically producing relatively coarse fibers in large quantities while formating and comingling relatively fine fibers simultaneously. The fine fibers tend to pad or cushion the coarse fibers in a manner minimizing or eliminating inter-abrasion of the fibers, thus greatly prolonging the life of products formed from the fibers.

There were 15 claims and 13 references cited in this patent.

Forming And Collecting Fibers. Patent No. 2,753,598. Filed January 4, 1954. Issued July 10, 1956. Two pages drawings; none reproduced. Assigned to Owens-Corning Fiberglas Corp. by Games Slayter.

An apparatus is provided for attenuating bodies of heat-softenable material to fibers through the utilization of a high velocity gaseous blast. It continuously removes the fibers from the blast on a rapidly moving surface adapted to convey the fibers to a conveyor for collection into a mat. The apparatus also includes a means for conducting the spent gases of the blast and the blast-induced air stream away from the fiber collection zone to facilitate the formation of a mat having a substantially smooth surface and of uniform thickness throughout its area.

Thus, through the utilization of the novel method of fiber formation, collection of the fibers, and subsequent deposition of the fibers in a mat formation, in a relatively quiescent zone, the resulting mat is of uniform thickness and wrinkles and irregularities in the mat surface are avoided. It is to be understood that the method has utility wherein blasts of steam or compressed air are employed in lieu of intensely hot blasts.

There were 3 claims and the following references were cited in this patent: 1,765,025, Miller, June 17, 1930; 2,188,373, Pearce, Jan. 30, 1940; 2,450,914, Powell, Oct. 12, 1948; 2,450,916, Coss et al., Oct. 12, 1948 and 2,489,243, Stalego, Nov. 22, 1949.

Sheet and Plate Glass

Conveyor Structure For Flat Glass Edging, Beveling. Patent No. 2,754,956. Filed May 2, 1951. Issued July 17, 1956. Four pages drawings; none reproduced. Assigned to Sommer & Maca Glass Machinery Co. by Kurt Sommer.

This invention relates to conveyor structure or mechanism for flat glass edging, beveling and polishing apparatus.

A new and improved gripping device is provided for use in the new conveyor mechanism. In use it will effectively but resiliently and yieldably grip the lateral or side faces of flat glass as the latter are fed upright into place between the endless conveyor mechanisms. The flat glass sheets are firmly but resiliently held against lateral or sidewise motion or vibration during their advancing movement through the machine, while a lower edge portion is being subjected to the edging, beveling and polishing actions of the respective wheels.

A novel construction for mounting the gripping devices with the endless conveyor chains which are embodied in the new endless conveyor mechanisms, is also provided.

There were three claims and the following references cited in this patent: 1,660,350, Owen, Feb. 28, 1928; 1,728,647, Weber, Sept. 17, 1929; 1,911,961, Melnick, May 30, 1933; 2,038,150, Weber, Apr. 21, 1936; 2,236,751, Dine, Apr. 1, 1941 and 2,551,332, Moore et al., May 1, 1951.

Cleaning Device For Glass Polishing Tools. Patent No. 2,753,707. Filed July 9, 1952. Issued July 10, 1956. Two pages drawings; none reproduced. Assigned to Les Glaceries De La Sambre Societé Anonyme by Edmond Laverdisse.

In the course of polishing of glass, the felt becomes

(*Continued on page* 222)

Hot molybdenum ingots are forged into round billets, then further processed to make 1¼ inch diameter electrodes for glass melting furnaces.

Fansteel

Molybdenum Electrodes for electric melting...

here's what they cost:

Based on actual operational costs covering a production of 16,027 tons of flint glass over a period of several months, electrode cost amounted to *only 2½ cents per ton!*

here's what you get:

1. Increased production (10 to 30%)
2. Longer furnace wall life
3. Improved glass quality

FANSTEEL ELECTRODES CAN BE INSTALLED WITHOUT FURNACE SHUT-DOWN . . . are 99.9% pure, give off a colorless oxide, have high thermal and electrical conductivity, and high temperature strength. Write for more complete information.

FANSTEEL METALLURGICAL CORPORATION
NORTH CHICAGO, ILLINOIS, U. S. A.

K 563

Current Statistical Position of Glass

Employment and Payrolls: Employment in the glass industry during January, 1957 was as follows: *Flat Glass*: A preliminary figure of 30,500 for January 1957 indicates a decrease of 2.6 per cent from the adjusted 31,300 reported for December, 1956. *Glass and Glassware, Pressed and Blown*: A decrease of 3 per cent is shown by the preliminary figure of 80,600 for January, 1957 when compared with the 83,100 figure of December, 1956. *Glass Products Made of Purchased Glass*: The preliminary figure of 15,500 indicates a drop of 3.7 per cent from the previous month's figure of 16,100.

GLASS CONTAINER SHIPMENTS

(All Figures in Gross)

Narrow Neck Containers

	Feb., 1957
Food	892,000
Medicinal and Health Supplies	1,349,000
Chemical, Household and Industrial	760,000
Toiletries and Cosmetics	784,000
Beverage, Returnable	452,000
Beverage, Non-returnable	63,000
Beer, Returnable	70,000
Beer, Non-returnable	438,000
Liquor	746,000
Wine	315,000
Sub-total (Narrow)	5,869,000

Wide Mouth Containers

Food	*2,742,000
Medicinal and Health Supplies	426,000
Chemical, Household and Industrial	182,000
Toiletries and Cosmetics	232,000
Packers' Tumblers	88,000
Dairy Products	158,000
Sub-total (Wide)	3,828,000
Total Domestic	9,697,000
Export Shipments	202,000
TOTAL SHIPMENTS	9,899,000

*This figure includes Fruit Jars and Jelly Glasses.

GLASS CONTAINER PRODUCTION AND INVENTORY

(All Figures in Gross)

		Production Feb., 1957	Stocks Feb., 1957
Food, Medicinal and Health Supplies; Chemical, Household and Industrial; Toiletries and Cosmetics	Narrow Neck	4,091,000	5,632,000
	Wide Mouth	*3,958,000	*5,073,000
Beverage, Returnable		737,000	1,571,000
Beverage, Non-returnable		82,000	179,000
Beer, Returnable		148,000	422,000
Beer, Non-returnable		547,000	795,000
Liquor		817,000	1,296,000
Wine		370,000	655,000
Packers' Tumblers		104,000	135,000
Dairy Products		203,000	349,000
TOTAL		*11,057,000	16,107,000

*This figure includes Fruit Jars and Jelly Glasses.

Payrolls in the glass industry during January, 1957 were as follows: *Flat Glass*: A decrease of 4.0 per cent is shown in the preliminary $14,802,638.20, when compared with December, 1956 adjusted $15,462,170.26. *Glass and Glassware, Pressed and Blown*: A decrease of 2.6 per cent is shown in the preliminary $28,779,517.99, reported for January, 1957 when compared with the previous month's adjusted $29,528,134.91 figure. *Glass Products Made of Purchased Glass*: A preliminary figure of $4,728,533.01 was reported for January, 1957. This is a decrease of 4.0 per cent compared with the adjusted figure of $4,939,479.98 of the previous month.

Glass Container Production: Based on figures released by the Bureau of Census was 11,057,000 gross during February, 1957. This represents a decrease of 5.5 per cent from the previous month's production of 11,698,000 gross. During February, 1956, glass container production was 11,128,000 gross or .6 per cent over the February, 1957 figure. At the end of the first two months of 1957, glass container manufacturers have produced a preliminary total of 22,755,000 gross. This is 2.5 per cent over the 22,227,000 gross produced during the corresponding 1956 period.

Shipments of glass containers during February, 1957 decreased 4 per cent to drop to 9,899,000 gross. This is a decrease from January, 1957 shipments which were 10,312,000 gross. Shipments during February, 1956 were 10,172,000 gross or 2.8 per cent over February, 1957. At the end of the first two months of 1957 shipments have reached a total of 20,211,000 gross, which is 1.1 per cent over the 19,986,000 gross shipped during the corresponding period last year.

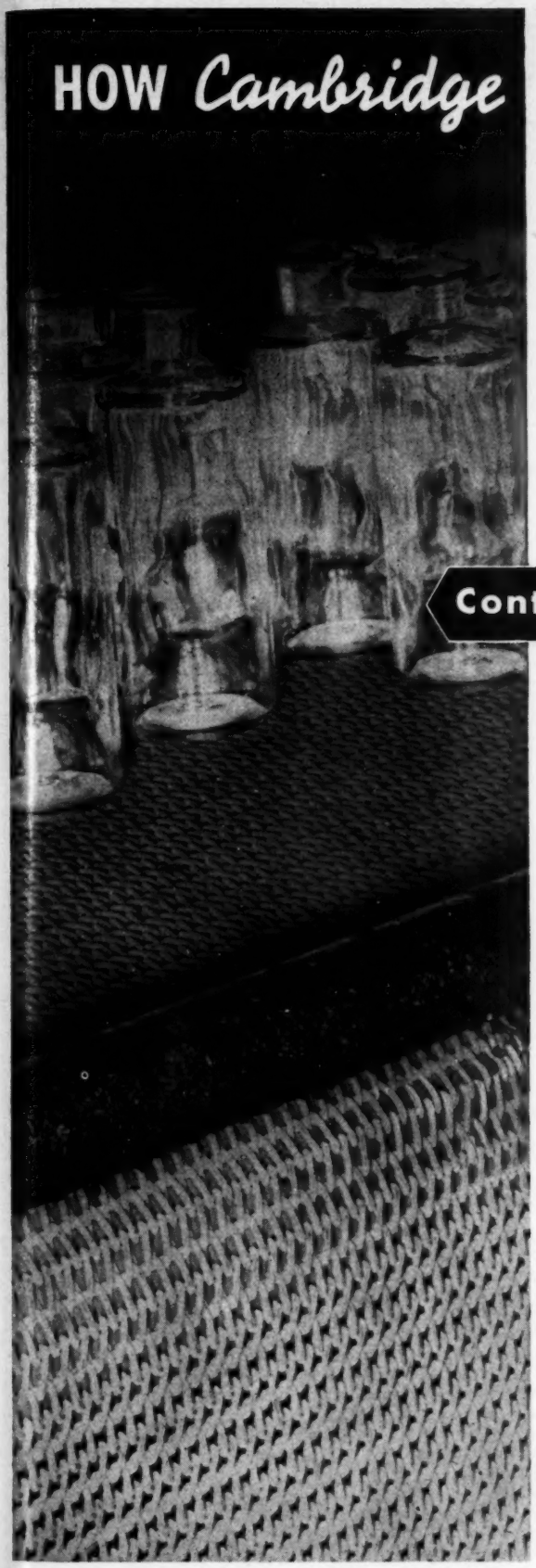
Stocks on hand at the end of February, 1957 were 16,107,000 gross. This is 7.6 per cent above the 14,976,000 gross on hand at the end of January, 1957 and 8.2 per cent higher than the 14,882,000 gross on hand at the end of February, 1956.

Automatic Tumbler Production: During January, 1957 was 6,042,000 dozen. This is a gain of 13.3 per cent against the January, 1956 production which was 5,332,000 dozen.

Shipments during January, 1957 rose to reach 4,689,000 dozen. This is 4.5 per cent higher than the 4,486,000 dozen shipped during January, 1956. At the end of the twelve months period ending January 31, 1957, shipments have reached a total of 54,836,000 dozen which is 11.7 per cent lower than the 62,128,000 dozen shipped last year.

Table, Kitchen and Household Glassware: Manufacturers' sales of machine-made table, kitchen and household glassware during January, 1957 reached 2,776,000 dozen. This is 9.7 per cent over the 2,531,000 gross of January, 1956. At the end of the twelve months period ending January 31, 1957, manufacturers had sold a total of 34,092,000 dozen, which was 8.2 per cent lower than the 37,024,000 dozen sold during the corresponding

(*Continued on page* 238)



WOVEN WIRE BELTS

help produce more uniform ware faster

Woven Wire Conveyor Belts save time and money by providing continuous processing in every phase of glass manufacture—molding, inspection, annealing, decorating and cullet removal. In a time-saving belt-to-belt flow through the plant, woven wire belts combine controlled movement of the ware—bottles, flatware, pharmaceutical vials and specialties—with processing. Need for trays and racks is eliminated, manual handling is minimized, and product uniformity and production efficiency are effectively increased. EXAMPLE:

Continuous Annealing

MOVING BELT carries hundreds of bottles through the lehr in a continuous stream after they are mechanically transferred from feeder belts. Woven wire feeder belts are preheated to reduce checking of ware as it is received hot from molding machines.

OPEN MESH of Cambridge belt allows free circulation of heat around the ware so that hot and cold spots are eliminated and each piece is uniformly heated.

ALL-METAL BELT withstands heat and flame curtain without damage, provides lasting strength because there are no seams, lacers or fasteners to break or wear. Wire belts are not cut by bits of broken glass in removal of cullet to crushers.

SPECIAL RAISED EDGES and surface attachments are available to hold even the smallest ware in position on the belt during flat or inclined movement.

Cambridge Woven Wire Conveyor Belts are made in any size, mesh or weave, from any metal or alloy, and can be used under a wide range of conditions . . . high temperatures, moderate heat or cold . . . wet or dry. Call your Cambridge Field Engineer to discuss how you can cut costs with continuous processing on woven wire conveyor belts. Look for his 'phone number under "Belting, Mechanical" in the Yellow Pages or write for FREE 130-PAGE REFERENCE MANUAL.

The Cambridge Wire Cloth Co.

Dept. K • Cambridge 4, Md.

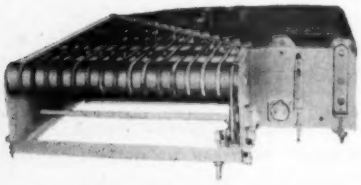
WIRE CLOTH | WOVEN WIRE CONVEYOR BELTS | WIRE CLOTH FABRICATIONS

OFFICES IN PRINCIPAL INDUSTRIAL CITIES

New Equipment and Supplies

FULL RIGHT ANGLE TURN FOR CONVEYOR SYSTEMS

Stewart-Glapat Corporation, 1639 Moxahala Avenue, Zanesville, Ohio has available the Stewart-Turn, which moves material on conveyors around corners of any degree up to a full right angle. Operation of the Stewart-Turn is based on a series of narrow belts running in grooved pulleys, meeting to provide an angular direction of flow. The belts are banked for constant contact with the material in motion, and positive belt guides prevent side sheer as the material changes direction.



A slight differential in speed between the bank of belts produces a positive turning action. Belt friction reaction to turning is eliminated by the design of the belts and their mountings. Belts are spaced to carry small as well as large or long articles. Parallel conveyor lines can be mounted side by side without the need of space-consuming radius turns, and converging conveyors can be fed into a single conveyor.

NEW HIGH SPEED DRILLING MACHINE

Sommer and Maca Glass Machinery Company, 3600 South Oakley Avenue, Chicago 9, Ill. has announced the "Somaca" High-Speed 4-Spindle Drilling Machine which is completely automatic. Construction of the machine is designed to drill from both sides of the glass to insure clean holes, free from chips. It can be adjusted to handle any thickness of sheet, plate, or laminated glass of any shape up to 36 inches square. The Somaca will automatically clamp the glass, drill two holes, and release the glass ten seconds after it is placed in the machine. Diamond core drills are used.

PACKAGED BURNERS

W. N. Best Combustion Equipment Company, Inc., 415 Eleventh Street, Carlstadt, N. J. offers its new "Calorex Planned-Package Burners" to be attached by bolting on. The packaged burners are made in a line of standard models to meet varying requirements. Top burner efficiency and automatic firing with any grade of fuel oil and changeover in minutes to gas when it is more desirable are among the features of the burners. Combustion performance of 12½ per cent CO_2 without smoke is guaranteed. It is said that consistent savings of one-fourth to one-third in fuel costs are reported by users. The automatic firing gives complete boiler room automation and results in labor saving costs in many installations.

TELESCOPING BELT CONVEYOR

Wilkie Company, 5520 Arch Street, Philadelphia 39, Pa. has just announced their telescopic belt conveyor which can transport goods in either direction, and eliminates manual carrying into or out of trailers and box cars because the telescopic feature permits the conveyor to follow the load. The conveyor is supplied in two, three or four sections; each section may be 10, 12, 14 or 16 feet long. Belt widths are 10, 20 or 30 inches. The belt on each section is driven by a separate motor and the conveyor itself is mobile and telescopes by power drive. Loads up to 300 lbs. per lineal foot are handled. Differences in level between loading dock and trailer bed are automatically accommodated due to the pivotal action between sections.

An elevating boom, which eliminates lifting, travels from the floor to 6 feet in height, and is optional. It may be located at either end and its elevation is controlled by pushbutton.

CATALOGS RECEIVED

American Lithium Institute, Inc., 84 Nassau Street, P.O. Box 549, Princeton, N. J., has prepared a 16-page booklet on lithium. The booklet lists the lithium chemicals, discusses their properties, applications, research possibilities, and availability. Copies may be obtained without charge from the Institute.

Minneapolis - Honeywell Regulator Company, Wayne and Windrim Avenues, Philadelphia 44, Pa. has released further Instrumentation Data Sheets. Sheet No. 11.5-4 describes fuel-air ratio control for single and alternate fuel systems and includes three diagrams and pictures of the instrumentation. Sheet No. 11.5-5 shows fuel-air ratio controls for combined fuel systems, also diagrammed. Instrumentation Data Sheet 10.18-12 explains how Sostman Motion Transducers can be used with any Brown ElectroniK instrument whenever linear or angular motion must be measured with a high degree of accuracy. Typical applications, performance data, and construction features are illustrated for both linear and angular motion types.

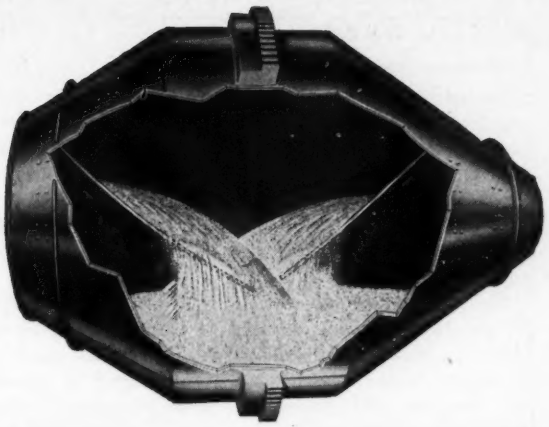
Pangborn Corporation, Hagerstown, Md. has prepared a 16-page illustrated reference bulletin, "Dust Control for Industry". Encompassing the complete range of dust control equipment and accessories, the new bulletin describes the importance of dust control to industry in relation to reduced maintenance costs, employee morale, and commercial utilization of dust by-products. The bulletin outlines standards of control and efficiency in dust collection, and lists the primary components parts of an engineered dust control system. A typical case history report demonstrates the benefits of dust control in handling a community relations problem. Drawings and photographs are used in conjunction with condensed descriptive information on the full line of engineered Pangborn dust control equipment. Copies of Bulletin No. 922 may be obtained direct from the corporation.

Hayward Scientific Glass Corporation, 217 Magnolia Avenue, Whittier, Cal. has a brochure on Hayward Fine Anneal, a glass said to have considerably less strain than Pyrex 7740, one of the most widely used types. To illustrate the differences between commercially annealed Pyrex and Hayward Fine Anneal through extreme degrees of temperature, the corporation secured the services of an independent testing laboratory. The photographic results of these tests and general specifications on Hayward Fine Anneal which is suitable for exacting scientific needs have been included in the brochure. A copy of this work and additional information on Hayward Fine Anneal may be obtained by writing to Department "K", at the company.

Fisher Scientific Company, 717 Forbes Street, Pittsburgh 19, Pa. has published a 16-page booklet entitled "Stirrers, Mixers & Shakers". There are dozens of different devices for accomplishing these laboratory operations quickly, efficiently, automatically. The booklet describes and illustrates these devices and includes prices.

Fisher & Porter Company, 812 Jacksonville Road, Hatboro, Pa., has published a new catalog describing the company's batch control systems. Copies of the new Catalog 91-109 are available on request from the company.

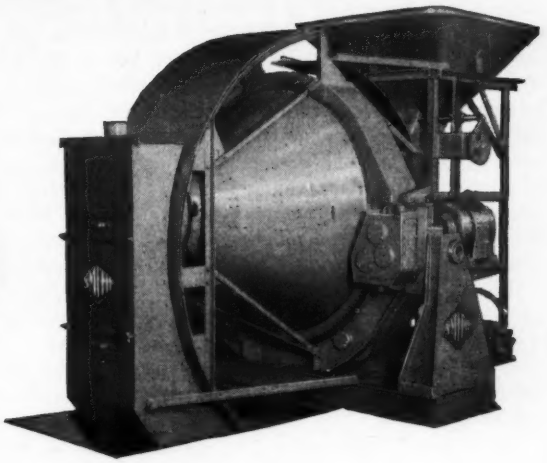
intimate mix



FACT 1: *Intimate mix* is the key to quality control in your batch plant.

FACT 2: *Intimate mix* is determined by correct counter-current action. This requires a duo cone-shaped drum with cross current blading to assure completely segregation-free batches.

FACT 3: The one batch mixer which gives the most intimate mix in the glass industry is the new Smith Tilting Mixer — *the only batch mixer with a duo cone-shaped drum and cross current blading unit.*



The only batch mixer providing a duo cone-shaped drum and cross current blading unit is a Smith Tilting Batch Mixer — the mixer which gives the most intimate mix in the glass industry.

Which size do you need:
30, 40, 60, 90, and 120 cubic feet.
(Each completely dust-sealed.)

THE T. L. SMITH COMPANY
Milwaukee 1, Wisconsin
Lufkin, Texas
Affiliated with Essick Manufacturing Company, Los Angeles, California

SMITH **batch mixer**

Inventions and Inventors . . .

(*Continued from page* 216)

progressively impregnated with polishing composition and the heat evolved by the friction causes evaporation of the water, the iron oxide dust remaining within the felt and gradually clogging the interstices. The disc hardens and becomes unsuitable for polishing. The polisher must then be withdrawn from the apparatus and subjected to washing with water and scraping with a brush, whereafter it is dried and may be reused.

This is not the case with the low polishers employed for the simultaneous polishing of the two faces of the glass. In this case, the abrasive mixture deposited on the upper face of the felt tends to descend by gravity into the mass and cannot be effectively extracted from there by brushing.

According to the present invention, the felt disc is subjected to the action of a vacuum after having been impregnated with water, which is preferably hot. The vacuum may be applied either to the surface of the felt in order to cause the polishing composition to rise to the surface, or through holes formed in the support of the felt in order to remove the polishing composition from the surface. The application of the vacuum may be intermittent and may alternate with the spraying of the felt, or the two operations may be carried out simultaneously. Prior to the application of the vacuum, it is advantageous to proceed with a superficial brushing.

The apparatus employed, according to the invention, may comprise a hood, which is fitted over the polisher to be cleaned and is connected to a vacuum pump, or a series of suction nozzles which are moved over the surface of the polisher, and which may alternate with sprinkling devices.

There were 2 claims and 10 references cited in this patent.

Sheet Glass Cutting Machine. Patent No. 2,746,153. Filed July 9, 1951. Issued May 22, 1956. Six pages drawings; none reproduced. Assigned to Libbey-Owens-Ford Glass Co. by Harry A. Kuntz.

This invention relates broadly to sheet cutting apparatus. More particularly, it has to do with an improved machine of the so-called template type upon which predetermined outlines can be rapidly, accurately and efficiently cut from sheets of glass or like materials.

This cutting machine comprises a supporting structure having associated with it a horizontal, flat table for supporting a sheet of glass during the cutting. Arranged above the table in vertically spaced relation is a horizontally disposed track template having the same configuration as the form or patterened outline to be cut from the sheet. Mounted upon the track and guided thereby is a cutting mechanism provided with a cutting wheel. The unit is adapted to travel around the template to score the glass sheet along any indicated line.

Means is provided for raising the table and glass sheet supported thereon, prior to the cutting operation and for maintaining them in elevated position during the cutting operation. Upon completion of the cutting operation, the table is automatically lowered and the sheet removed. Means is also provided for controlling the traversing speed of the cutting unit along the track template by means of an especially designed cam member which is rotated in synchronized relation to the movement of the cutting unit by a drive mechanism.

There were 12 claims and 11 references cited in this patent.

Tube and Cane Machines

Glass Articles. Patent No. 2,735,230. Filed January 10, 1952. Issued Feb. 21, 1956. Two sheets drawings; none reproduced. Vaughan Morrill, Jr.

In accordance with this invention, a process is provided in which a blank of glass tubing, the bore of which may be irregular and the wall thickness of which may vary from place to place, is shaped upon a mandrel or a succession of mandrels to produce a shaped blank having an accurately formed bore, and an enlarged section the internal dimensions of which are exactly known.

Two such enlarged sections may be produced in the same blank, one at either end. The enlarged sections produced by the profiled mandrel are open-ended and are shaped to allow the mandrel to be pulled therefrom. A tip may be formed on the stem of the blank while the mandrel is still in position or is partly withdrawn. When two enlarged sections are formed on the same blank, the stem portion intermediate the enlarged section may be divided. The enlarged sections may be trimmed to give each section a known desired capacity. Two enlarged sections, which need not be identical, but whose exterior dimensions should be practically identical at their open edges, are butted. If it is desired to insert an object within the bulb of the pipette to be made, that object need only be placed within one of the enlarged sections before those sections are finally butted. The butted enlarged sections are then fused together in such a way that the exterior dimensions of the finished pipette are the same as those of the unfused sections. By this process, a pipette is produced in which the volume is accurately known and predetermined, and in which the bore of the stem is so uniform that the pipette may be calibrated with a simple screen process.

There were 9 claims and the following references were cited in this patent: 1,699,305, Meyer, Jan. 15, 1929; 2,389,360, Guyer et al., Nov. 20, 1945; 2,392,104, Smith, Jan. 1, 1946; 2,396,635, Bogoslowsky, Mar. 19, 1946; 2,573,553, Doran, Oct. 30, 1951, and 409,283, Great Britain, Apr. 24, 1934.

Bulb Coating Method. Patent No. 2,740,726. Filed April 11, 1952. Issued April 3, 1956. No drawings. Assigned General Electric Co. by James T. Anderson.

According to the present invention a coating of silica is deposited on the surface of a foundation, such as the interior wall of the glass bulb of an incandescent lamp, by applying to the surface a solution of a resin and a colloidal solution of silica in a suitable solvent, such as alcohol or a mixture of solvents, allowing the coating to dry and wholly or in part removing the resin by heat.

The heating process also removes the last remains of the solvents and produces a fine whitish translucent coating of silica, suitable for light-diffusion uses.

First a colloidal solution of silica referred to as solution A, is prepared in the following manner.

200 cc. of pure tetra ethyl silicate is mixed with 210 cc. of acetone, 38 cc. of distilled water and 2 cc. of dilute

(*Continued on page* 238)

NEW . . .

a *free flowing* burned lime

After months of intensive research The Woodville Lime Products Company is pleased to offer the glass manufacturing industry

Doloroc Crystalyme

This latest development in lime processing means that glass manufacturers can now obtain a burned lime having measurably improved flow characteristics, reduced tendency to compress and a grain size specifically designed to match other glass batch materials.

In actual practice **Doloroc Crystalyme** provides the following advantages:

- **Easier handling**
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- **Reduction of batch segregation to an absolute minimum.**

The Woodville Lime Products Company has continuously produced high quality lime products for the past fifty-five years. It operates one of the largest low iron deposits of dolomite stone in the famous Northwestern Ohio field.

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Hamilton, Ohio

Bottle Blowers Convention . . .

(*Continued from page* 210)

Mr. Minton reported to delegates that it was, in his opinion, important for machinery be set in action for the creation of a Pan American Conference of Glass Workers. The prime purpose of such a conference would be to coordinate efforts in the field of collective bargaining techniques. The international president said that the present lower economic standards of certain South American glass workers could pose a potential threat to American glass workers through the importation of bottles made by cheap labor. "It is our duty as a Union," he said, "to attempt the elevation of living standards throughout the world. . . . We must, as a Trade Union, give aid and assistance wherever humanly possible. We must act with vigor in the building of free trade unions in this area in order that democracy can be strengthened and living standards improved."

Among the motions made and carried at the convention were a 50¢-a-month increase of dues and a 25¢-a-month levy for a strike fund. The strike fund will also be used to combat proposd legislation aimed at the heart of the glass industry. "Today there is before some state legislatures," warned Minton, "proposed laws that would bar our product from reaching the consumer."

In his plea for the setting up of a strike fund, Minton said, "we can expect and we will have strikes. We must, however, so plan our program so that strikes will be of a local nature and not of an international nature unless our Union is being destroyed."

Commenting upon labor-management relations in the glass industry, Minton said that there are still some employers who cannot now, nor will they ever, recognize equality, justice and progress. It is because of these employers, he said, that the Union needed a Defense Fund to protect its membership.

Minton, however, did pay tribute to other glass firms when he concluded, "In passing, I wish to compliment and pay tribute to some of our other employer groups. We have many fine employers who are interested in the welfare of their people and who are interested in developing a labor relations program in close cooperation with this Union. These employers have no fear of a Defense Fund."

Richard L. Chency, marketing director of the Glass Container Manufacturers Institute, gave a talk on the marketing program of the Institute to increase sales of glass containers, which was well received by the 630 delegates.

LANCASTER LENS COMPANY ACQUIRES CONTROLLING INTEREST IN INDIANA GLASS

The Lancaster Lens Company, Lancaster, Ohio, has acquired controlling interest in Indiana Glass Company, Dunkirk, Indiana, Robert K. Fox, president of Lancaster Lens, and George M. Morton, vice president of Indiana Glass announced recently.

Mr. Fox, now president of The Lancaster Lens Company, also becomes president of Indiana Glass Company. Mr. Morton becomes a vice president of both Companies. No changes in operating personnel are planned.

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FOR THE GLASS INDUSTRY

LANCASTER, OHIO U. S. A.

This Wissco Balanced Spiral Belt, in constant use 24 hours a day and five days a week, carries glass fiber mats through a 650°F drying oven at speeds up to 50 feet per minute.

WISSCO BELTS *and the Texas Glass Fiber Corporation*

The story of Wissco Belts is best told by their users. For instance, Texas Glass Fiber Corporation of Grandview, Texas, reports:

"The installation of a Wissco Belt speeded up our glass-curing operation by 250%!"

This Wissco Belt is used in drying glass fiber mats impregnated with phenolic resin bonding material. The company's president, Mr. W. E. Hutton-Miller, reports: "Before we switched to Wissco Belts, this operation slowed up our production considerably.

"With our old, close-mesh belt, the lack of adequate circulating air greatly retarded the maximum flow rate through our drying oven. For instance, in drying glass air filter material, the greatest speed possible was 10 feet per minute. What's more, dripping resin continually clogged the small mesh holes, making it necessary to remove these deposits by banging the belt with a hammer. This, of course, did not do the life expectancy of the belt any good.

"Then a Wissco technical representative visited Texas Glass Fiber. He recommended that we change to an open-mesh Wissco Balanced Spiral Belt. Not only did the open mesh of this belt enable the fiber glass material to dry faster, but it also prevented dripping resin from clogging the belt.

"As a result, we were able to increase our belt speeds for air filter drying to 35 feet per minute. We find Wissco Belts superior in every respect to the belts we formerly used. In addition to increased production, these belts have brought us definite maintenance and replacement savings," Mr. Hutton-Miller concludes.

So—no matter what kind of operation yours is—it'll pay you to get the complete story on Wissco Belts, as well as free Wissco technical help, from our nearest sales office soon.

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WICKWIRE SPENCER STEEL DIVISION
Atlanta • Boston • Buffalo • Chicago • Detroit • New Orleans • New York • Philadelphia
CF&I OFFICES IN CANADA: Montreal • Toronto

CF&I **WISSCO BELTS**
PRODUCT OF WICKWIRE SPENCER STEEL DIVISION
THE COLORADO FUEL AND IRON CORPORATION

4548

Milestones in Glass Progress

PHOTO COURTESY THE TOLEDO MUSEUM OF ART

1715 This fine example of a German "pokale," or covered goblet—produced about 1715-1720—measures 17½" from the base to tip of cover. Much of this glass was very heavy because of the style of decoration, deep-cut so that the glass would not easily slip through the fingers.

1890 Michigan Alkali Company, now a division of Wyandotte Chemicals Corporation (South Plant, above), was founded by Captain J. B. Ford to supply Soda Ash to the glass industry. Wyandotte has grown up with glass. Today, as in the past, it is a working partner, supplying technical assistance and raw-material chemicals to those great companies marking milestones in glass progress.

Wyandotte CHEMICALS

Michigan Alkali Division, Wyandotte Chemicals Corporation
Wyandotte, Michigan • Offices in principal cities

Founded by a Glassmaker to Serve the Glass Industry

Batch Materials . . .
(*Continued from page* 195)

CaO	7.42
MgO	.03
BaO	.58
Na_2O	12.07
K_2O	1.69
SO_3	.24
F_2	.86
	100.40
$-O_2$ correction F_2	.40
	100.00

Converting this to 15.3% of the total slag, we find the oxide contribution from the dust.

SiO_2	11.40%
Al_2O_3	.50
CaO	1.10
SO_3	.04
Alkali	2.20
BaO	.10
F_2	.13

If the three sources of flux materials are now added together, the predicted composition of the slag is obtained which is very comparable to that actually found by analysis.

	3% Brick	81.7% Na_2SO_4	15.3% Dust	Calculated	Actual
SiO_2	.21%		11.4%	11.6%	11.9%
Fe_2O_3	.18			.18	.20
Al_2O_3	.30		.5	.8	.55
CaO	.05		1.1	1.15	1.08
MgO	1.97			1.97	1.94
Cr_2O_3	.26			.26	.25
SO_3	.03	46.0	.04	46.07	46.08
Alkali	—	35.7	2.2	37.9	37.7
BaO	—		.1	.1	.5
F_2	—		.13	.13	.04

The agreement between calculated and the actual slag analysis is almost too good but is typical of many such treatments made in the past during the course of this study.

It is interesting to note that if the sample is taken from the top of the checkers as in the first example, the alkali sulfate component is absent and only the brick and theoretical dust analysis need be considered. This is understandable as the sample is above the point where soda condensation occurs.

CONCLUSIONS

An effort has been made to show the importance of chemical and especially physical characteristics of raw materials used in glass batches. Some techniques of evaluating various factors dependent upon these characteristics have been illustrated. It is believed with additional experience and data, a more thorough understanding of the importance of physical characteristics of batch materials on furnace life and glass quality will come, and with this knowledge, a better operation will result.

Annual A.C.S. Meeting . . .

(*Continued from page* 196)

of Glass Technology, University of Illinois, continues as Secretary of the Glass Division.

On the technical side the Society as a whole has exceeded all past performances in programming one hundred and ninety-seven papers, the largest number ever to be crowded into an Annual Meeting.

Frank R. Bacon, Owens-Illinois Glass Company, Toledo, Ohio, Program Committee chairman of the Glass Division, has provided an interesting list of twenty-two papers, two less than were presented last year.

Following is a list of the papers in their order of presentation to be given at the Glass Division sessions:

1. Stress Measurement in Circular Cylinders. Paul M. Sutton, Corning Glass Works, Corning, N. Y.
2. Measurement of Stress Optical Coefficient and Rate of Stress Release in Commercial Soda-Lime Glasses. A. F. Van Zee and H. M. Noritake, Owens-Illinois, Toledo, Ohio.
3. Elastic Properties of Glasses. Harold T. Smyth, Rutgers University, New Brunswick, N. J.
4. Effect of Thermal History on Glass Expansion Characteristics. H. E. Hagy and H. N. Ritland, Corning Glass Works, Corning, N. Y.
5. Dielectric Loss and the States of Glass. D. W. Rinehart, Pittsburgh Plate Glass, Creighton, Pa.
6. Compaction Variations in Heat-Treated Plate Glass. D. W. Rinehart, Pittsburgh Plate Glass.
7. Some Notes on the History of Tempered Glass. Alexander Silverman, University of Pittsburgh, Pittsburgh, Pa.
8. Intimate Mixing in Glass Batch Preparation. Robert P. Bremner, T. L. Smith Company, Milwaukee, Wis.
9. Fundamental Studies on the Glassmelting Process. I. Reaction Mechanisms in the Dissolution of Silica by Silicate Melts. C. L. McKinnis, Owens-Corning Fiberglas Corp., Newark, Ohio, and J. W. Sutton, Denison University, Granville, Ohio.
10. Glass Flow through Continuous Tanks. A. R. Cooper, Massachusetts Institute of Technology, Cambridge, Mass.
11. Optical and Physical Properties of Some Calcium Aluminate Glasses. H. C. Hafner, N. J. Kreidl, and R. A. Weidel, Bausch & Lomb Optical Company, Rochester, N. Y.
12. Constitution of Sodium, Potassium, and Lithium Phosphate Glasses. A. E. R. Westman, Ontario Research Foundation, Toronto, Ontario, Canada, and P. A. Gartaganis, Dow Chemical of Canada, Ltd., Sarnia, Ontario.
13. Glass Formation and Properties of Glasses in the System Na_2O-B_2O_3-SiO_2-TiO_2. J. H. Strimple, National Lead Company, South Amboy, N. J. and E. A. Giess, Alfred University, Alfred, N. Y.
14. Study of the Surface Durability of Container Glasses. H. E. Simpson, State University of New York, College of Ceramics, Alfred University, Alfred, N. Y.
15. Inhibition of Alkaline Attack on Soda-Lime Glass (Contribution of the University of Toledo). George A. Hudson, Mobay Chemical Company,

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Grefco fire clay brick are recommended for the lower portions of the checker settings, the lower regenerator walls, the rider tile and for lining the flues.

Grefco silica brick, for caps and breast walls, are uniform and of highest quality, and are available in standard or super duty grade.

You will find one or more Grefco plants ready to supply each major glass producing district at minimum transportation costs.

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GENERAL REFRACTORIES

New Martinsville, W. Va., and Frank R. Bacon, Owens-Illinois, Toledo, Ohio.

16. Detection of Reaction Products Between Water and Soda-Lime Silica Glass. Franklin Fu-Yen Wang, Glascote Products, Inc., Cleveland, Ohio, and F. V. Tooley, University of Illinois, Urbana, Ill.
17. Influence of Reaction Products on Reaction Between Water and Soda-Lime-Silica Glass. Franklin Fu-Yen Wang, Glascote Products, Inc., Cleveland, Ohio, and F. V. Tooley, University of Illinois, Urbana, Ill.
18. Diffusion of Argon in Potassium-Lime-Silica Glass. M. B. Reynolds, General Electric Knolls Atomic Power Laboratory, Schenectady, N. Y.
19. Gaseous Diffusion Under Stress in Glass and Alumina. K. D. McAfee, Bell Telephone Laboratories, Murray Hill, N. J.
20. Studies on Wettability of Platinum by Molten Sodium Silicate. M. L. Volpe, R. M. Fulrath, and J. A. Pask, University of California, Berkeley, Cal.
21. Activities in Borosilicate Melts: II, Some Mixtures of Calcium Borates-Calcium Silicates, W. J. Knapp, University of California, Los Angeles, Cal., and H. Flood, Institute of Silicate Science, Norwegian Institute of Technology, Trondheim, Norway.
22. Structrual Interpretation of Immiscibility in Oxide Systems III: Effect of Alkalies and Alumina in Ternary Systems. Ernest M. Levin and Stanley Block, National Bureau of Standards, Washington, D. C.

On the social side, attending members will be afforded true Texas style entertainment; a "chuck wagon" dinner, followed by the annual floor show at the Dallas State Fairgrounds. Bus tours of "Old Mexico" and an air trip to Mexico City will be added attractions.

For the ladies, there will be a luncheon in the Empire Room of the Statler-Hilton, a style show by Neiman Marcus, and a sightseeing tour of Dallas.

PENNSYLVANIA GLASS SAND ANNOUNCES 1957 SCHOLARSHIP AWARDS

Again this year, Pennsylvania Glass Sand Corporation will present Merit Award Scholarships to twelve ceramic engineering schools. Each scholarship provides full tuition for the senior year in ceramic engineering and will be awarded to the junior student attaining the highest scholastic average at each school for the junior year's work.

Merit Award Scholarships for the 1957-58 school year will be offered to the following schools: Alfred University, Clemson College, Georgia Institute of Technology, Iowa State College, Ohio State University, Pennsylvania State University, Rutgers University, University of Illinois, University of Missouri, University of Texas, University of Washington, and Virginia Polytechnic Institute.

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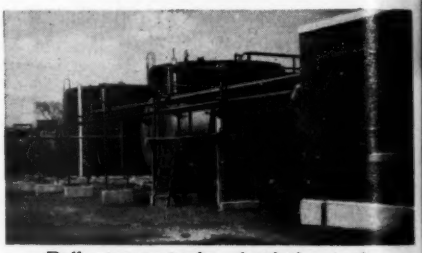
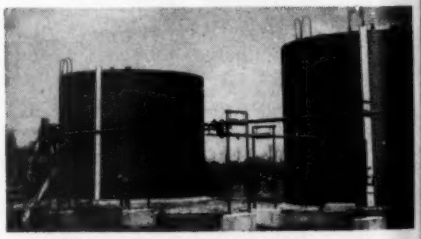


Bulk storage tanks, circulating tanks and pump house, all TECO engineered.



Bulk storage tanks with interconnecting, unloading and transfer lines.

Shutdowns due to curtailment of natural gas have proved costly to many manufacturers in the past.

On the other hand, glass melting plants where precautionary wisdom has been exercised are no longer plagued with fuel supply problems.

★ TECO can design the complete system from bulk unloading station, up to the oil burner on the furnace.

★ TECO designed systems have been installed in some of the largest glass plants in the country.

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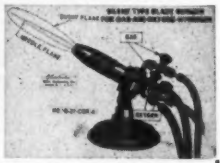

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AMERICAN WINDOW GLASS TO FORM COMPANY WITH SAINT GOBAIN

Otto G. Schwenk, president of American Window Glass Company, has disclosed plans for the company to join with Saint Gobain of Paris, world's oldest and one of the largest producers of plate glass, in forming a new, completely integrated glass producing firm in the United States. First details of the proposed new company were in the report to stockholders. Under terms of the agreement, reached after several months' negotiation, the Blue Ridge Glass Corporation of Kingsport, Tennessee, a wholly-owned subsidiary of Saint Gobain and a producer of rolled and structural glass, would combine with American, which operates three sheet glass plants and one safety glass laminating plant in the U.S.

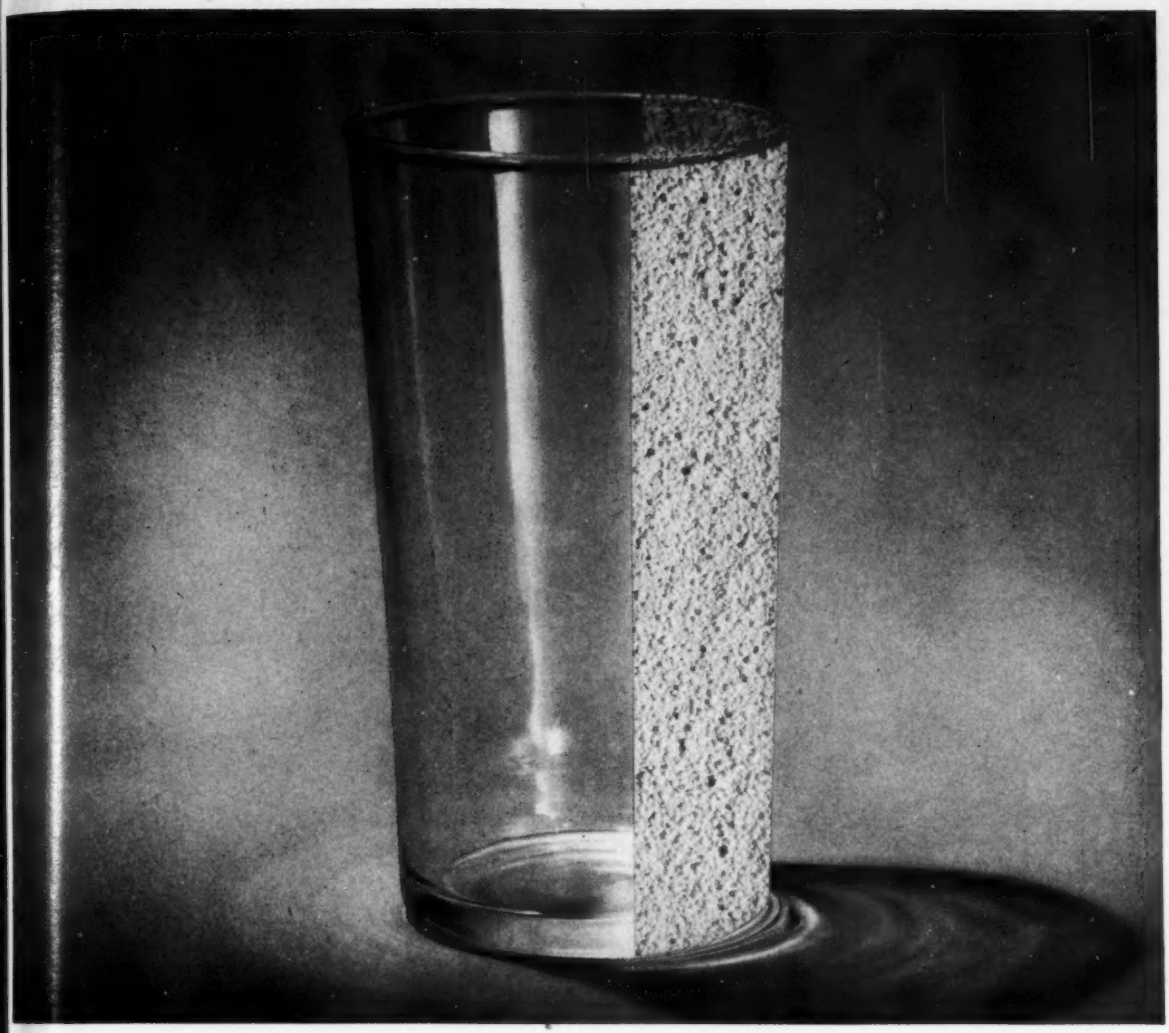
Pointing out that the absence of plate glass from the produce line was a major factor limiting American's earnings, Mr. Schwenk told stockholders that the new company proposes to build a modern plate glass facility in the U.S. using the latest Saint Gobain production techniques. The addition of this plant would give the new company manufacturing facilities for a complete line of flat glass products, including plate, window, rolled, structural, and laminated safety glass.

Mr. Schwenk reported that the consolidation is subject to approval of French and U.S. government agencies, and after such approval, the proposal will be submitted to the shareholders.

American, chartered in 1899, is the third largest sheet glass producer in the U.S. and by this move will enter the plate glass producing ranks for the first time. Saint Gobain has produced plate glass since its inception in 1665 and is noted for its extensive use of twin-grinding and its current development of twin-polishing.

American reported 1956 net sales of $23 million, up 5 per cent over 1955 volume. During 1956 the company placed in operation its new furnace for the production of gray glass and is now completing another new furnace for production of tinted specialty glass. During the period from mid 1956 to mid 1957, American will have also repaired its four clear glass furnaces.

• H. Dean Menoher, manufacturing vice president of American Window Glass Company, was elected a director of the company, filling a vacancy on the Board. Mr. Menoher has been with the company for 45 years.



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Japanese Concepts . . .

(*Continued from page* 208)

When glass is cooled slowly the stored surface energy will decrease by the amalgamation of holes to larger ones.

If, however, glass is quenched leaving no time for the amalgamation of holes the number of larger ones would be at least negligibly small. The non-existence of larger holes would probably be the reason for the high strength of glass fibers.

Furthermore, the enormous amount of stored energy at the hole surface of intensively quenched glass would cause the volume change of glass even at the temperature as low as 200-300°C.

In this brief review of the current concepts of glass structure in Japan the writer hopes that our efforts in exploring the structure of glass will contribute not only to the theories being currently advanced in other countries, but also, be of help in our constant research on structure of glass.

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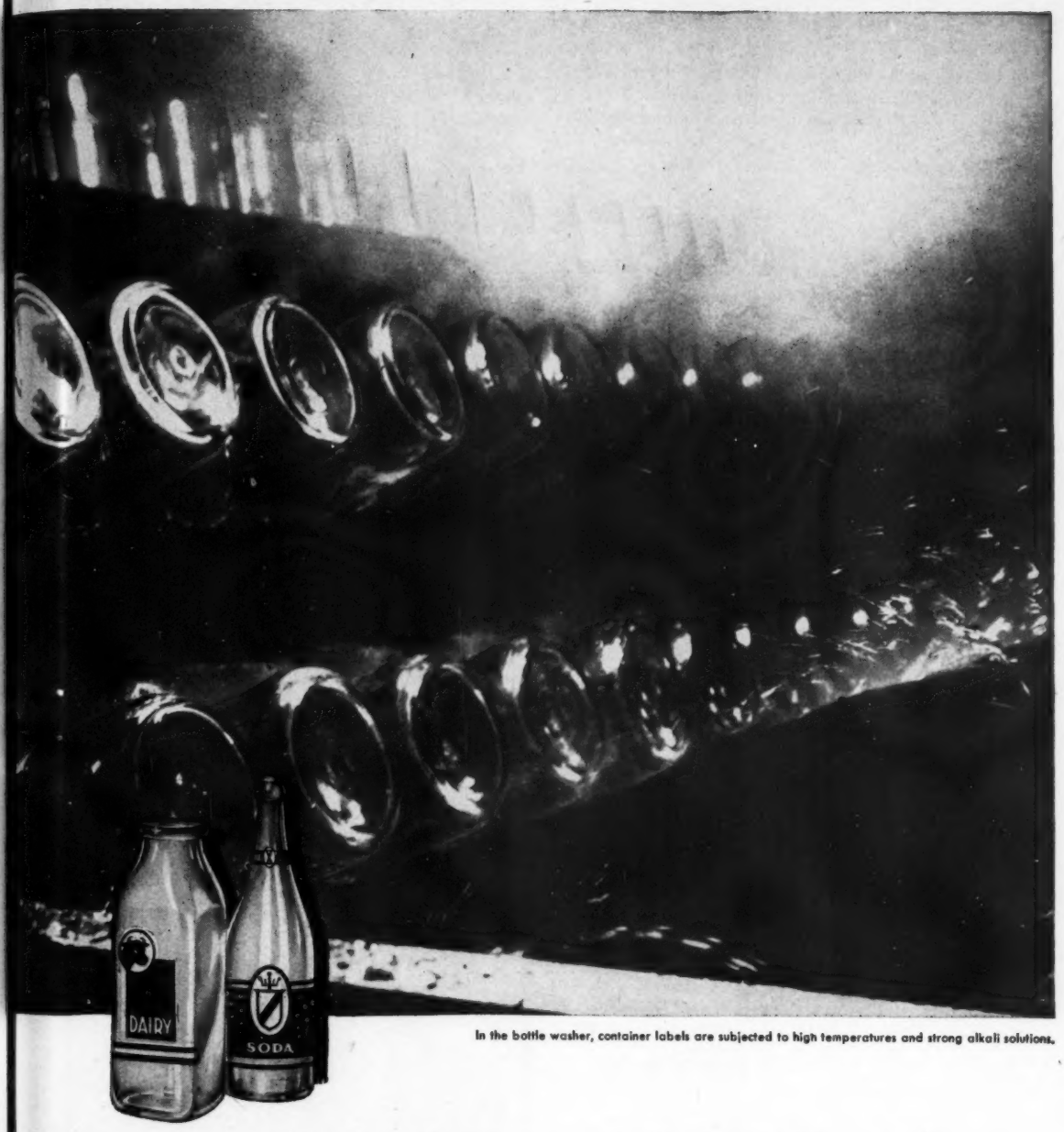
WOODVILLE TO PRODUCE DOLOMITIC LIME FOR INDUSTRY

J. R. Cowell, Jr., of The Woodville Lime Products Company Toledo, Ohio, announces that the company plans to concentrate its efforts on the manufacture and production of burned dolomitic lime for the glass industry. Mr. Cowell further stated that he felt improvements in burned lime for glass were long overdue and that his company has plans for a product that should prove of valuable assistance in the making of higher quality glass. Such properties as flow characteristics and the tendency to compact are being studied with the view toward making these more nearly like other glass raw materials.

Glass Technicians, Inc., of Hamilton, Ohio, will handle sales and engineering work in the glass industry for the Woodville Company. This firm is presently engaged in glass consulting work and numbers among its staff, Robert W. Hopkins and William H. Manring, veterans in the glass container industry and officials of The Calumite Company.



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AMERICAN LITHIUM INSTITUTE LAUNCHES RESEARCH PROGRAM

The American Lithium Institute has initiated a program of sponsored research on lithium alloys at Massachusetts Institute of Technology and on lithium-containing glass at Pennsylvania State University. The Institute will also establish fellowships at the two institutions.

Marshall Sittig

The announcement of the research projects and fellowships was made by Marshall Sittig, president and managing director of the newly formed Institute.

At Penn State, Dr. W. A. Weyl of the College of Mineral Industries will direct a contract-research program to determine the fundamental behavior of the lithium ion in glass. It is hoped that this will shed light on one or more of the beneficial effects lithium has on glass: increase in strength, improvement in electrical properties, and improvement in optical properties. The actual laboratory investigations will be carried out by Dr. Sigmund Urnes, who is a Norwegian glass technologist. He will be assisted by the A.L.I. fellow-to-be.

In detailing the need for such information, Mr. Sittig gave as an example the commercial use of lithium in TV picture tubes, where it contributes to increased strength as well as light weight. Learning more about the "why" of such applications will provide fundamental knowledge that may stimulate applied research on the use of lithium for other specific glass products with specialized properties.

Sponsoring such projects as these two studies is one of the two principal functions for which the American Lithium Institute was formed last November. The other is collection and dissemination of technical information on lithium and its compounds. Since a technical library is already being set up at the Institute offices in Princeton, N. J., and several publications are under preparation, the MIT and Penn State projects put the new organization into full-scale operation, Mr. Sittig stated.

Member companies of the American Lithium Institute, Inc. are the three major U.S. lithium producers—American Potash and Chemical Corporation, Foote Mineral Company and Lithium Corporation of America.

CHARLES D. RAU RETIRES

At the annual stockholders' meeting of Fairmount Glass Works it was announced that Charles D. Rau has retired as Chairman of the Board. Elected to office were John R. Harkness, president, Cedric C. Rau, first vice president, John H. Rau, Jr., vice president and Clayton B. Johnson, secretary-treasurer.

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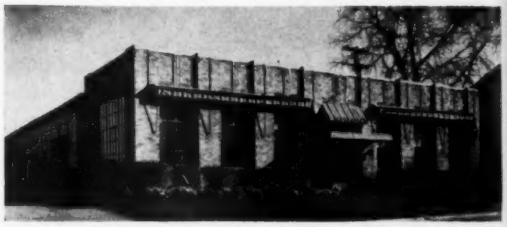

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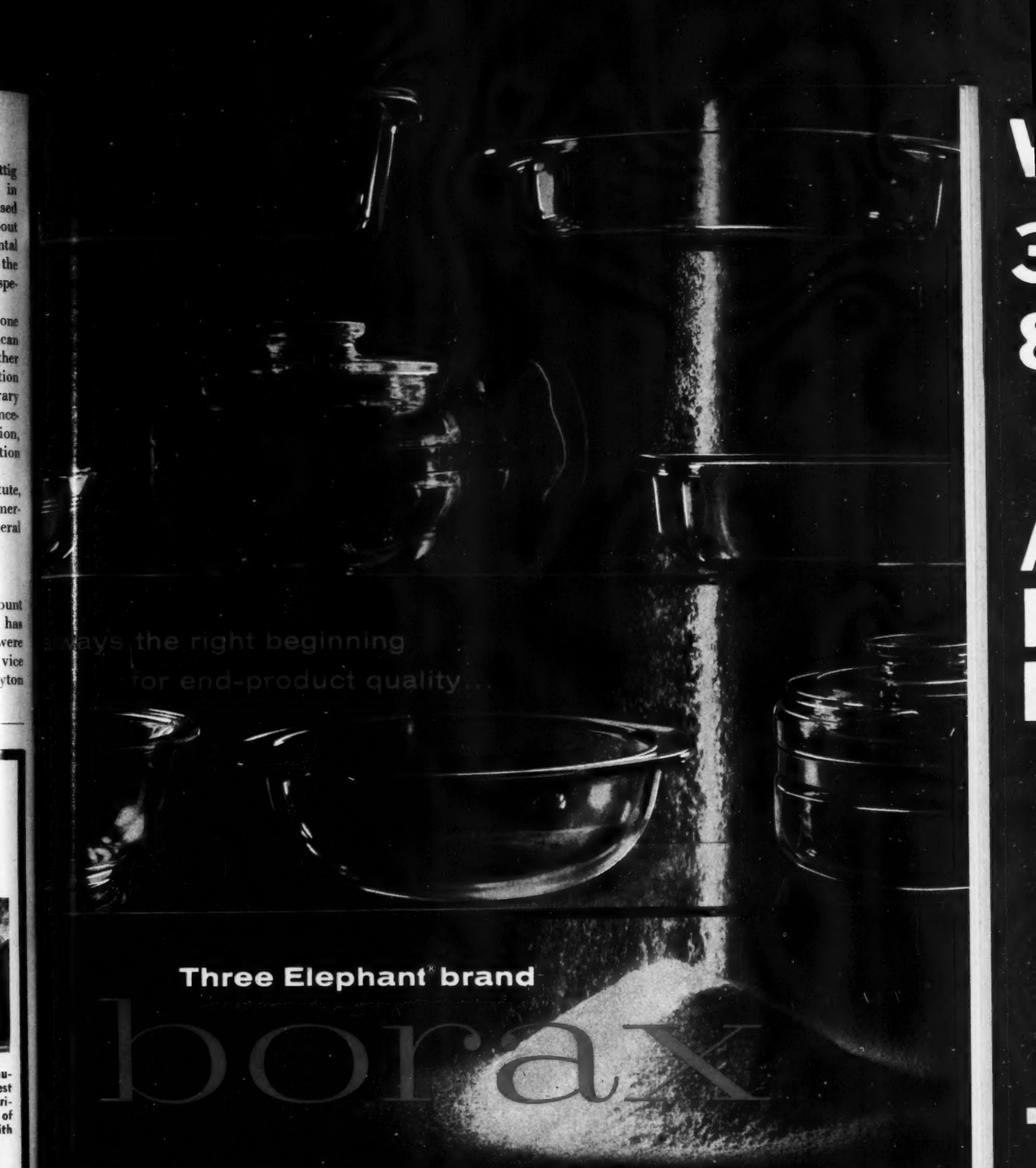

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